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PROCESS IMPROVEMENT STUDIES
on the
BATTELLE HYDROTHERMAL COAL PROCESS

by

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16. ABSTRACT The report gives results of a study to improve the economic viability of the Battelle Hydrothermal (HT) Coal Process by reducing the costs associated with liquid/solid separation and leachant regeneration. Laboratory experiments were conducted to evaluate process improvements for (1) separating the spent leachant and residual sodium from the coal product, (2) reducing the moisture content of the coal product, and (3) regenerating the leachant. In addition, coal desulfurization experiments were performed and economic studies were conducted to evaluate the impacts of process improvements on coal desulfurization costs. By using -20 and -50 (rather than -200) mesh coal and other process modifications, significant process improvements were realized. Separation rates were increased manyfold by adding dispersants. The moisture content of the coal product was lowered to about 40% by centrifugation. Sodium was effectively washed from the coal product by saturated lime water. Using countercurrent washing, the optimum washing circuit was composed of four disc filter stages, six belt filter stages to separate spent leachant and sodium from the clean coal, and a centrifuge stage to dewater the coal. Several regenerates were found to be effective in removing greater than about 85% of the total sulfide sulfur from the spent leachant: iron carbonate was the leading candidate.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Coal	Stationary Sources	08G, 21D
Desulfurization	Hydrothermal desulfurization	07A, 07D
Leaching		
Sodium	Liquid/Solid Regeneration	07B
Calcium Oxides		

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ABSTRACT

This report presents the results of a study to improve the economic viability of the Battelle Hydrothermal Coal Process by reducing the costs associated with liquid/solid separation and leachant regeneration.

Laboratory experiments were conducted to evaluate process improvements for (1) separating the spent leachant and residual sodium from the coal product, (2) reducing the moisture content of the coal product, and (3) regenerating the leachant. In addition to these laboratory investigations, coal desulfurization experiments were performed and economic studies were conducted to evaluate the impacts of process improvements on coal desulfurization costs.

Through the use of -20 and -50 mesh coal rather than -200 mesh coal and through other process modifications, significant process improvements were realized. Separation rates were increased many-fold upon the addition of dispersants. The moisture content of the coal product was lowered to about 40 percent by centrifugation. Sodium was effectively washed from the coal product by saturated lime water. Employing countercurrent washing, the optimum washing circuit was composed of four disc filter stages, six belt filter stages to separate spent leachant and sodium from the clean coal, and a centrifuge stage to dewater the coal.

A number of regenerates were found to be effective in removing greater than about 85 percent of the total sulfide sulfur from the spent leachant. Iron carbonate was the leading candidate with up to 99 percent removal of the sulfide sulfur in less than 15 minutes depending on the Fe/S ratio and source of $FeCO_3$.

Total processing costs (1978 dollars), are estimated to range from $38/ton of product coal for hydrothermal desulfurization of a typical Eastern coal to $10 for desulfurization of a Western coal. These costs include profit, interest and tax costs of $10 and $4/ton for the eastern and western product coals, respectively. Total costs for a combined physical/hydrothermal process which cleans high sulfur Eastern coal is estimated to be $24/ton of product coal.

The process improvements evaluated would provide only marginally lower costs than those for present processes when considering high sulfur coal. However, replacement of evaporators in the washing section with reverse osmosis units could potentially reduce costs by $2 to $3/ton. Furthermore, the use of a leachant regeneration process similar to the citrate flue gas desulfurization process culd reduce costs by $5 to $7/ton. Direct combustion of coal without drying in coal-water mixtures could reduce product cost by $4/ton. These options require further laboratory research for verification.

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CONVERSION FACTORS

The EPA policy is to express all measurements in metric units. Implementing this practice will result in additional costs and lack of clarity. Generally, this report uses English units of measure. For conversion to the international system (SI) of units, use the following conversion factors.

TABLE OF CONVERSION FACTORS

Multiply English Unit	By Conversion	To Obtain SI Units
pound/hour	0.454	kilogram/hour
British thermal unit	0.252	kilogram - calories
British thermal unit/pound	0.555	kilogram - calories/kilogram
ton (short)	0.907	metric ton (1000 kilograms)
pounds/square inch (gauge)	(0.06805 psig +1)(a)	atmospheres (absolute)
inch	2.54	centimeters
feet	0.3048	meters
degree fahrenheit	$(5/9)(^{\circ}F-32)$(a)	degree Celcius
gallon	3.785	liters
ton/year	0.907	metric ton/year
pounds/million, British thermal unit	1.8×10^{-6}	kilogram/kilogram-calories
pound	0.454	kilogram
square inches	6.452	square centimeters
mesh number(a,b)	8	2.36 mm
	20	850 μm
	50	300 μm
	70	212 μm
	100	150 μm
	200	75 μm
	325	45 μm

(a) Actual conversion, not a multiplier

(b) Mesh numbers correspond to U.S.A. Standard Sieve Series as specified by ASTM-E-11-70.

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CONCLUSIONS AND RECOMMENDATIONS

Results from a previous study for the U.S. Environmental Protection Agency - Combustion of Hydrothermally Treated (HTT) Coals, indicated that, in many instances, HTT coals can be burned with little or no sulfur emissions and with improved combustion properties. The objectives of subsequent work discussed in this report were to: (1) improve the economic viability of the hydrothermal coal process by reducing the cost of leachant regeneration and liquid/solid separation, and (2) determine the potential of using this process for cleaning coal to comply with SO_2 emission regulations.

Through the use of coarser coals (-20 and -50 mesh as compared to -200 mesh) and other process modifications, significant process improvements in the liquid/solid separation segment can be realized. Separation rates can be increased by a factor of 10 by adding 0.5 lb of a dispersant/ton of coal processed. Sodium, an undesirable contaminant from the HTT process, can be effectively removed from the coal product with a reasonable number of washing stages using saturated lime water as the washing medium. Wash-water consumption is minimized by employing countercurrent slurry washing. The moisture content of the coal product is reduced from approximately 60 percent to approximately 40 percent by employing centrifugation. Furthermore, the mineral matter content is reduced to below that of the raw coal during the desulfurization step and subsequent downstream processing. The final product is a solid fuel with a reduced mineral matter content and acceptable sodium content, that contains less than the equivalent of 1.2 lb $SO_2/10^6$ Btu, and is impregnated with a sulfur scavenger. Previous work indicates that this coal product can be burned with little or no sulfur emission.

A number of methods were found to be effective in regenerating the spent leachant for recycle by the removal of the sulfide sulfur. Of the regenerates evaluated, zinc oxide, ferrous and ferric hydroxides, reduced activated ferric oxide, and ferrous carbonate effectively removed essentially all or a major portion of the sulfide sulfur from the spent leachant.

Employing the process improvements developed under this program, total costs (1978 collars) costs for a self-contained hydrothermal treatment plant processing 400 ton/hr of coal is estimated to range from $38/ton of product coal for desulfurization of a typical Eastern coal, for example, a Pittsburgh seam coal, to $10/ton of product coal for treatment of a Western (subbituminous) coal. These costs include profit, interest, and taxes which are estimated at $10/ton and $4/ton, respectively.

Some coals, i.e., those containing low concentrations of organic sulfur and high concentrations of pyritic sulfur, can be physically cleaned to produce a low-sulfur coal which will meet the 1971 Federal Sulfur Emissions Standards of 1.2 lb of $SO_2/10^6$ Btu for coal-fired steam generators. However, physical cleaning at these low specific gravity conditions is not effective because of the small fraction of coal recovered from the process. To make the process economically feasible, the waste stream must be cleaned to produce a "middling" product that can be used in compliance with less stringent SO_2 emission standards. An alternative would be to use a combined physical-hydrothermal process. In the combined process, residue from the low specific gravity separation would be chemically cleaned to meet the 1.2 lb $SO_2/10^6$ Btu emission limit.

Economic evaluation of a combined physical-hydrothermal treatment plant producing 595 tons/hour of cleaned coal (375 tons by the hydrothermal process and 200 tons by physical cleaning) indicated the operating costs to be approximately $24/ton product coal, which includes capital related costs, profit, interest, and taxes.

The above costs do not include any credit for sulfur capture by the calcium in the HTT coal during combustion. Previous work for U.S. Environmental Protection Agency (Contract No. 68-02-2119) indicated that approximately 50 to 100 percent of the sulfur remaining in the HTT coals was captured during combustion of the calcium impregnated coals in a 1 lb/hr and a 50 lb/hr pulverized coal combustion unit. Thus, the HTT coals could be a source of a solid fuel that would meet the planned revised sulfur emissions standards. However, testing on a larger scale should be conducted to confirm sulfur capture in scale-up.

Some additional areas of investigation which are recommended include:

- Replacement of evaporators with reverse osmosis units might reduce water purification costs in the washing section. Membrane resistance to the pH of such solutions must be investigated. Potential savings are \$2.00 to \$3.00 per ton of coal produced.

- Precipitation of sulfur from the leachant by a process similar to the citrate flue gas desulfurization process. This would require some chemistry and process studies, but could save \$5 to \$7 per ton of coal in regeneration costs.

- Studies in washing at near the same temperature as sulfur leaching. This could reduce the number of washer stages from the current 13 required stages.

Positive results of such process studies could bring the costs of treating Westland coal, for example, more into line with those normally reported for flue-gas desulfurization.

Project Objectives

Preliminary results of a program sponsored by EPA - "Combustion of Hydrothermally Treated Coals" (Contract No. 68-02-2119) - indicated that the HTT coals prepared by the Battelle Hydrothermal Coal Process (BHCP) from selected coals are clean solid fuels that potentially can be burned with little or no sulfur emissions control. Sulfur oxide concentration in the flue gases was well below the 1971 New Source Performance Standards (NSPS). Also, the HTT coal was found to have improved combustion characteristics in terms of ignition, flammability, and carbon burnout. Trace metals emissions should be significantly reduced because of lower concentrations in the HTT coals. Therefore, the use of this clean, solid fuel in conventional boilers and furnaces ought to reduce environmental pollution.

Original plans on the project reported here called for additional assessment of the combustion characteristics of HTT coal firing. However, cost studies completed as the project was starting indicated that the HTT process probably would not be competitive with flue gas desulfurization unless process improvements were made to reduce costs. Therefore, the scope of project work was changed and the efforts were directed toward the development of process improvements, process performance data, and process cost estimates with which to determine the potential of using the HTT process for cleaning coal to comply with SO_2 emission regulations.

- Improve the economic viability of the HTT process by evaluating methods to reduce the cost of leachant/coal separation, coal dewatering, and leachant regeneration, and

- Determine the costs of using the HTT process for cleaning coal to comply with SO_2 emission regulations.

This report covers the study results in three major sections:

- Liquid/solid separation and washing
- Leach regeneration and coal desulfurization
- HTT cost studies.

LIQUID/SOLID SEPARATION AND WASHING

Background

In earlier, internally sponsored work, Battelle had conducted an experimental investigation on separation of spent leachant from hydrothermally treated (HTT) coal, with simultaneous removal of residual sodium. Preliminary filtration rates, settling rates, cake and thickener underflow solids contents, and washing efficiency data were generated. From these data, a liquid/solid (L/S) separation-washing circuit was devised. The circuit consisted of five disc filter stages in series with a final solid bowl centrifuge. Countercurrent washing was used. From data obtained in this investigation, along with other available data, the cost of desulfurizing coal by the Battelle Hydrothermal Coal Process (BHCP) was calculated to be \$31.56/ton (see Table 1). Costs for the washing and separation section were the highest. Therefore, in this overall effort to increase the economic viability of the Battelle Hydrothermal Coal Process (BHCP), an investigation was undertaken to reduce the costs of the L/S separation segment.

First, the L/S separation costs were separated into seven cost components, as summarized in Table 2. Analysis of these costs indicated that the most significant components were moisture penalty, chemical costs, and capital related expenses. Two factors, moisture content of the HTT coal and separation rate, had the greatest effect on the magnitude of these cost components. Therefore, the greatest emphasis in this part of the study was directed toward improving the coal/leachant separation rate while achieving good sodium removal from the cleaned coal and reducing the final coal moisture content. The study objective was to obtain an optimum tradeoff between cost and process capabilities -- minimize cost while maintaining acceptable levels

TABLE 1. COST OF MIXED-LEACHANT BATTELLE HYDROTHERMAL COAL PROCESS(a)

Plant Section	Contribution to Price, \$/ton(b) (1976 dollars)
Reactor	5.82
Washing and Separation	9.71
Regeneration	5.25
Sulfur Recovery	3.39
Offsites	7.39
Total	31.56

(a) Reference: Development of the Battelle Hydrothermal Coal Process, p. 107, July 30, 1976.

(b) Processing cost does not include cost of raw coal.

TABLE 2. WASHING AND SEPARATION COSTS FOR THE MIXED-LEACHANT BATTELLE HYDROTHERMAL COAL PROCESS(a)

Cost Components	Contribution to Selling Price, \$/ton(b)
Make-up Chemicals-NaOH	1.66
Treated Coal	0.97
Utilities	0.26
Direct Labor Related	0.21
Capital Related	1.13
Moisture Penalty	3.83
Contribution to Operating Cost	8.06
Profit, Interest, Income Tax	1.65
Total	9.71(c)

(a) Reference: Ref. 1.

(b) First Quarter, 1976 dollars; based on the following treatment conditions: Water/Coal=2, NaOH/Coal=0.16, Lime/Coal=0.05, Reaction Time=10 min, Reaction Temperature-275 C, Washwater/Coal=2.

(c) Total processing cost, including \$18.00/ton for raw coal, was \$49.60/ton.

of sodium and moisture in the cleaned coal. From the data generated, the optimum washing and separation circuit was developed.

APPROACH

The separation and washing section interacts strongly with the rest of the BHCP. Hydrothermally Treated Coal (HTT coal) leaving the separation section contains treated coal, moisture, residual treatment chemicals, and spent leachant. The excess moisture must be removed either before or during utilization of the clean coal; the lost chemicals must be made up. The quantity of spent leachant, which is dependent on the water-to-coal ratio used in the reactor, the wash water-to-coal ratio, and quantity of leachant removed with the product coal, determines the evaporator and regeneration section loads. Makeup of chemicals is determined by the washing efficiency of each separation stage and the number of stages. The washing efficiency is affected by the quantity of residual moisture and chemicals in the HTT coal. Therefore, the selection of the optimal separation and washing circuit is a complicated tradeoff of a number of cost-sensitive variables within the framework of the separation system (i.e., minimum moisture content of HTT coal obtainable per type of separation equipment. maximum separation rate obtainable per washing stage per type of separation equipment, minimum sodium removal levels, etc.). The tradeoffs can be evaluated in terms of individual cost components as in Table 2.

Because of the large scale of the planned application and the treated coal characteristics, separation and dewatering by vacuum filtration and centrifugation was selected for intensive study. The effects of coal particle size were investigated and the use of filtration aids, surfactants, and oil agglomeration to improve separation rates and final cake moisture were examined. Two types of washing methods were investigated for each of the two separation systems - displacement washing and repulp washing. Separation and washing alternatives are discussed in detail in Appendix 1.

Because of the complex nature of the separation and washing circuit and its interactions with other cost sensitive sections of the BHCP, a computer program was prepared to investigate the relationships between the total separation and washing costs and the following processing variables.

1. Separation equipment
2. Separation rate
3. Cake solids content
4. Washwater-to-coal ratio
5. Number of washing stages
6. Residual unbound sodium.

Sensitivity studies allowed rapid investigation of the different separation techniques and indicated where the most significant cost savings could be obtained.

SUMMARY

The investigation led to significant technological achievements and economic inplications relating to the vacuum filtration and centrifugal filtration systems and washing methods.

Vacuum Filtration

Through the use of coarser coals (-20 and -50 mesh coal as compared to -100 mesh), high NaOH and CaO concentrations, and specialized washing techniques, significant process improvements were realized.

Separation Rate. When the original -20 mesh solution was tested, a rate of only 0.008 ton/hr/ft^2 was obtained. Pretreatment testing was first conducted to improve the rate. The use of flocculants resulted in floating of the fines, allowing the coarser material to settle. Consequently, the fines settled on the surface of the cake, resulting in an effective barrier to further dewatering. Dispersants (sodium lauryl sulfate was found most effective) were found to solve this problem by dispersing the fines throughout the cake. Separation rates were increased by a factor of 10 to 0.08 ton/hr/ft^2 at an addition level of 0.5 lb dispersant/ton.

After the initial dispersant addition, separation rate was found to depend primarily on the degree of washing, increasing after each wash until it leveled off at >0.6 ton/hr/ft^2. In addition, the degree of washing also had a strong effect on the final moisture content of the coal product. Results with -20 and -50 mesh HTT coal are summarized in Table 3.

TABLE 3. SEPARATION RATE AND MOISTURE CONTENT OF VACUUM FILTRATION SEPARATED HTT COAL SLURRY AS A FUNCTION OF COAL PARTICLE SIZE

Particle Size, Mesh	20 x 0		50 x 0	
Degree of Washing	Separation Rate[(a)] ton/hr/ft^2	Moisture Content, Percent	Separation Rate[(a)] ton/hr/ft^2	Moisture Content Percent
Primary Separation	0.09	53	0.08	48
First Wash	0.12	53	0.23	59
Second Wash	0.24	54	0.33	50
Third Wash	0.46	54	0.47	51
Fourth Wash	0.59	55	0.59	52

(a) Separations employed using 0.5 lb of the dispersant sodium lauryl sulfate/ton of coal.

Moisture Removal. The original separation tests with -20 mesh coal produced a cake with ≈59 percent moisture. The use of dispersants for separation rate improvement also improved the moisture removal efficiency during separation. The cake showed lower moisture retention with the smaller -50 mesh coal. However, this trend to lower moisture retention with smaller particle sizes did not extend downward to -100 mesh coal where ≈60 percent moisture cakes were produced. Since the separation rates with the -50 mesh coal were not significantly less than with the -20 mesh coal, this size range seemed near optimal for further development work.

Other measures to further reduce the moisture content included oil agglomeration prior to separation and solvent displacement. The oil agglomeration tests showed that increased separation rates of 1.9 tons/hr/ft^2 could be obtained; however, the moisture content of the clean coal was increased by only 1 to 3 percent. A washing test with a mixture of toluene and ethyl alcohol was conducted on a high moisture extensively washed cake. The solvents effectively displaced the water from the cake but did not reduce the moisture content of the coal product. Drying tests with the solvent washed coal showed that drying energy requirements were only half those for water washed coal.

Centrifugal Filtration

Centrifuge testing data, combined with vendor supplied data, provided the basis for the separation rate and cake moisture content used in the system design. Combined with the data from the filtration section, the centrifugation data were used to design the optimal washing circuit. The results of work on separation rate and moisture removal capability along with a proposed washing circuit are summarized separately below.

Separation Rate. Based on screen-bowl centrifuge equipment employed for coal processing of similarly sized coal, a separation rate of approximately 50 tons dry solids/hr/machine (based on the largest equipment) commercially available) has been estimated. No experiment rate tests were conducted (because of the small size of the test equipment), but it is known from theory that the rate is inversely proportional to the liquid viscosity. Therefore, the rate of separation should be improved by higher temperatures. In addition, higher slurry solids concentration should also increase the separation rate.

Moisture Removal. Tests were conducted to establish the moisture content of the centrifuged HTT coal cake and determine the effect of dispersant additions and oil agglomeration. The tests showed that washed coal and unwashed HTT coal produced a cake containing approximately 42 percent moisture. Washing appeared to add little additional moisture to the product cake. The addition of dispersant to the washed coal slurry resulted in cake with approximately the same moisture content. The dispersant addition, however, did result in greater solids recovery and better centrate clarity. Oil agglomeration, like the dispersant addition, did little to the cake moisture content, but did improve solids recovery and centrate clarity.

Combined Separation System.

Since the moisture content was not reduced to below 38 percent (the moisture level established by the cost simulation model as the dividing point between an economically superior all-filter or all-centrifuge system) by centrifugal separation, the economics favor a filtration system. However, a combined system with a series of filters for washing followed by a final centrifuge stage appears to be superior to an all-filtration system.

Washing

The residual sodium in the treated coal must be reduced for economic reasons (for sodium recycle and reuse), as well as combustion (corrosion) considerations.

The washing scheme developed for HTT coal consisted of a number of countercurrent working separation stages in series using repulp washing. Displacement washing methods were found to have low separation rates and high costs.

Tests showed that saturated lime water wash was clearly superior to washing with water or saturated CO_2 water. Apparently the dissolved calcium in the lime water promoted more effective exchange with the sodium. In fact, the bound sodium (sodium not removable by extensive wash) was lowered from ≈ 0.5 to ≈ 0.1 percent. This result was especially significant since it allowed removal to the desired 0.5 percent total sodium level with a reasonable number of washing stages.

Since the process goal is desulfurization, the converted sulfur in the product should be reduced to less than 1.2 lb $SO_2/10^6$ Btu by washing. At sufficiently high caustic leachant concentration levels, the sulfur content of the washed coal was consistently brought below the 0.9 percent (MAF) sulfur level. Also, previous studies have shown that the high residual calcium level (>2.6 percent MF calcium), combined with the residual sodium, lead to increased sulfur capture in the ash, making the combustion off-gas even lower in SO_2 than anticipated solely from the coal's fulfur content.

The ash composition and content of the product coal are also important characteristics, affecting both boiler design and operation. Through the use of appropriate separation and washing techniques, the ash can be selectively reduced to a level approximately equal to that in the raw coal. Since both the sodium and calcium content of the treated coal are higher than in the starting coals, the reductions in ash are due to ash solubilization and removal during the desulfurization and subsequent downstream processing steps.

RESULTS AND DISCUSSION

Results of the liquid/solid separation and washing investigations for each of the two separation systems and for the two washing techniques, follow. Theoretical economic considerations for the separation systems are included.

Vacuum Filtration

The vacuum filtration program was designed to determine the effects of various processing variables on filtration operation in order to design the best separation system. The problem was first studied through a computerized simulation model (Appendix 2) to determine those variables with the greatest influence on costs. The model results were utilized by directing the experimental program into two areas: (1) improved separation techniques designed to increase filtration rates and solid contents of HTT coal and (2) improved washing techniques to more efficiently remove the dissolved sodium from the HTT coal.

Theoretical Economic Considerations. The simulation model allowed the determination and efficient investigation of the most inportant process variables. These variables included

- The number of washing stages
- Washwater/coal ratio
- Bound and unbound sodium levels
- Solids content of washed HTT coal.

The model contained two parts. In part one, the residual sodium levels with fixed feed solution concentration, washwater-to-coal ratio, and filter cake solids content for 1 to 40 washing stages were calculated. In part two, the operating cost (including capital amortization) for the separation and washing circuit was calculated.

To examine the importance of the various process variables, four plots were constructed:

- Costs versus filter cake solids content (Figure 1)
- Costs versus unbound sodium level (Figure 2)
- Costs versus washwater-to-coal ratio (Figure 3)
- Various cost components versus the process variables (Figure 4).

These data made it clear that the filter cake solids content was a very important factor. Total costs increased as much as $2/ton as the moisture content rose from 48 to 52 percent. The washwater-to-coal ratio was also an important variable with a relatively sharp curve and a definite minimum. Over a reasonable washing range, e.g., w = 1.5 to 2.5 lb washwater/lb dry solids, the cost varied as much as $1.50/ton. The cost for removal of unbound sodium also showed a relatively sharp curve with a pronounced minimum. The upturn in costs was especially sharp, increasing in the range of very low residual dissolved sodium levels. From the final curve, it was clear that (1) for a fixed filtration rate, the total capital costs are not strongly

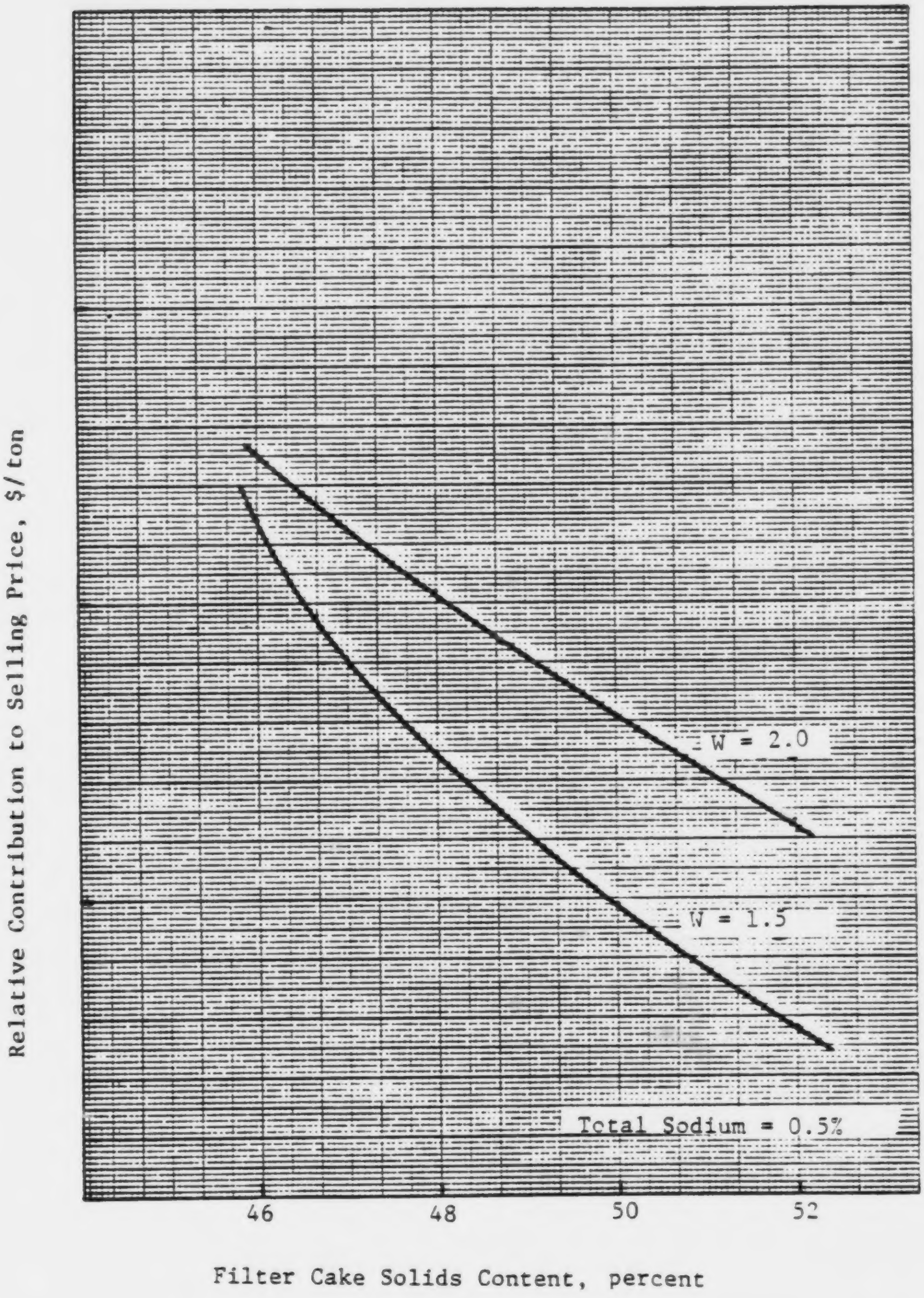

FIGURE 1. FILTRATION SEPARATION AND WASHING COSTS VERSUS FILTER CAKE SOLIDS CONTENT AS A FUNCTION OF WASHWATER-TO-COAL RATIO

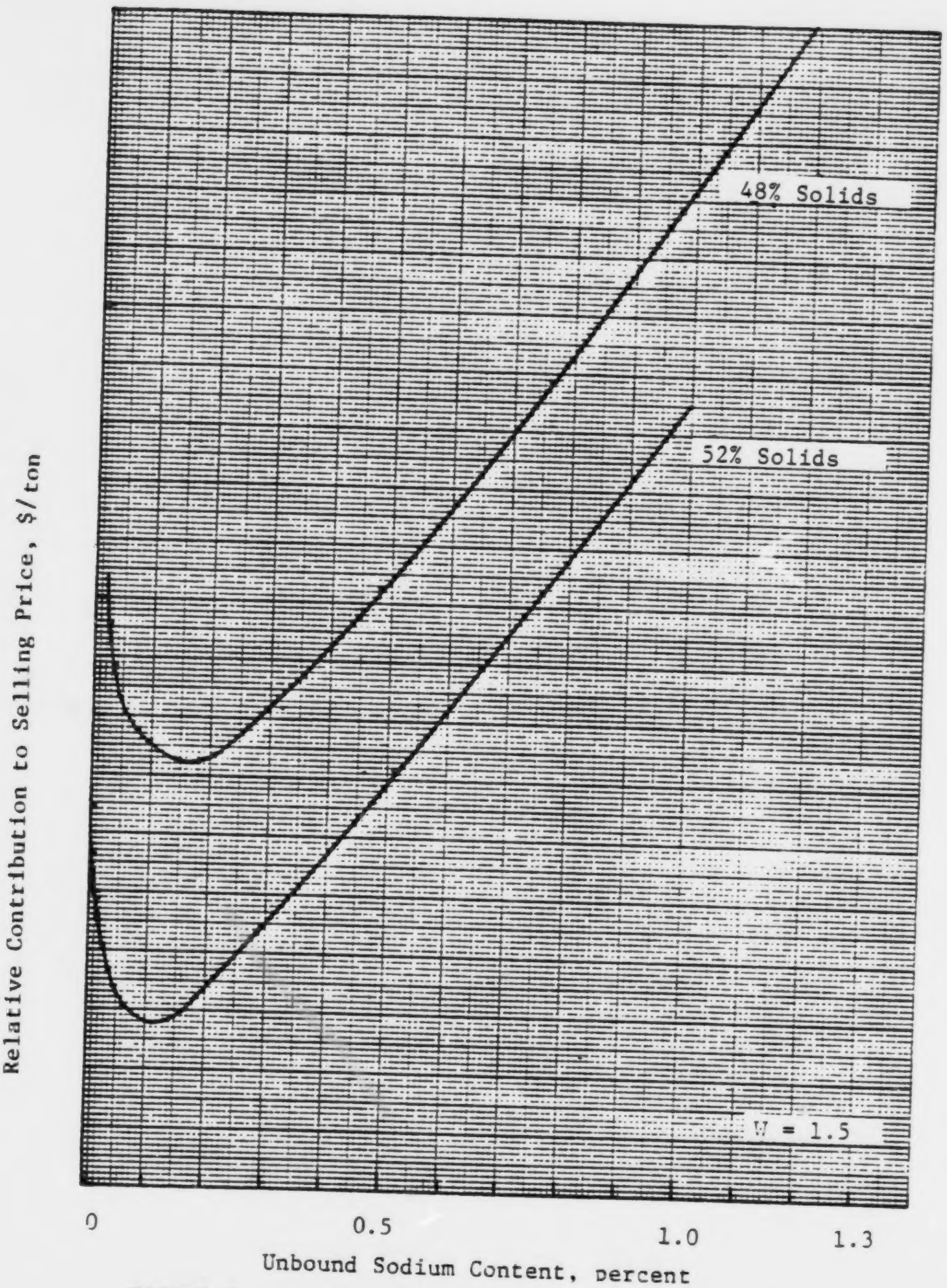

FIGURE 2. FILTRATION SEPARATION AND WASHING COSTS VERSUS UNBOUND SODIUM CONTENT OF THE FINAL WASHED CAKE AS A FUNCTION OF FILTER CAKE SOLIDS CONTENT

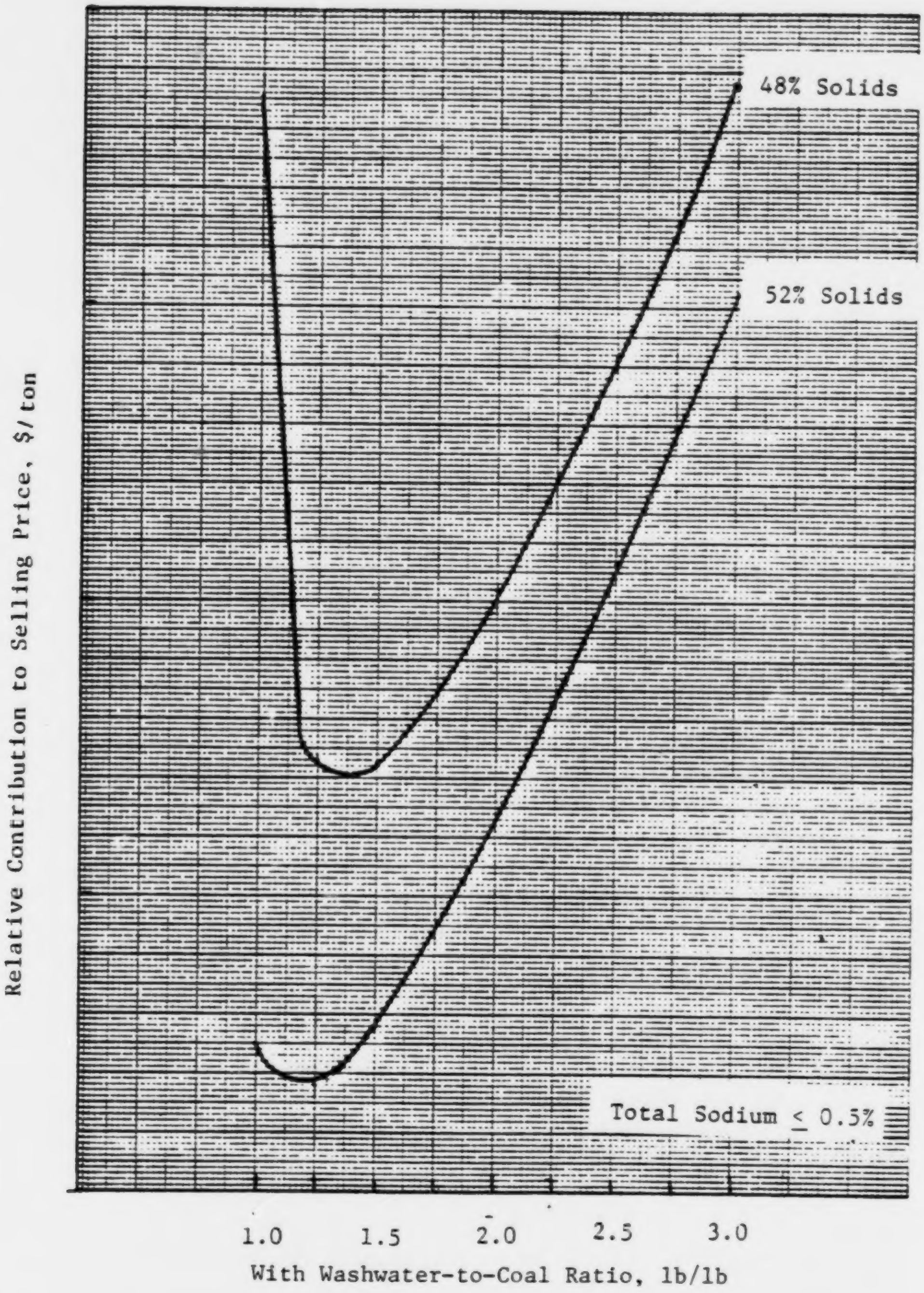

FIGURE 3. FILTRATION SEPARATION AND WASHING COSTS VERSUS WASHWATER-TO-COAL RATIO AS A FUNCTION OF FILTER CAKE SOLIDS CONTENT

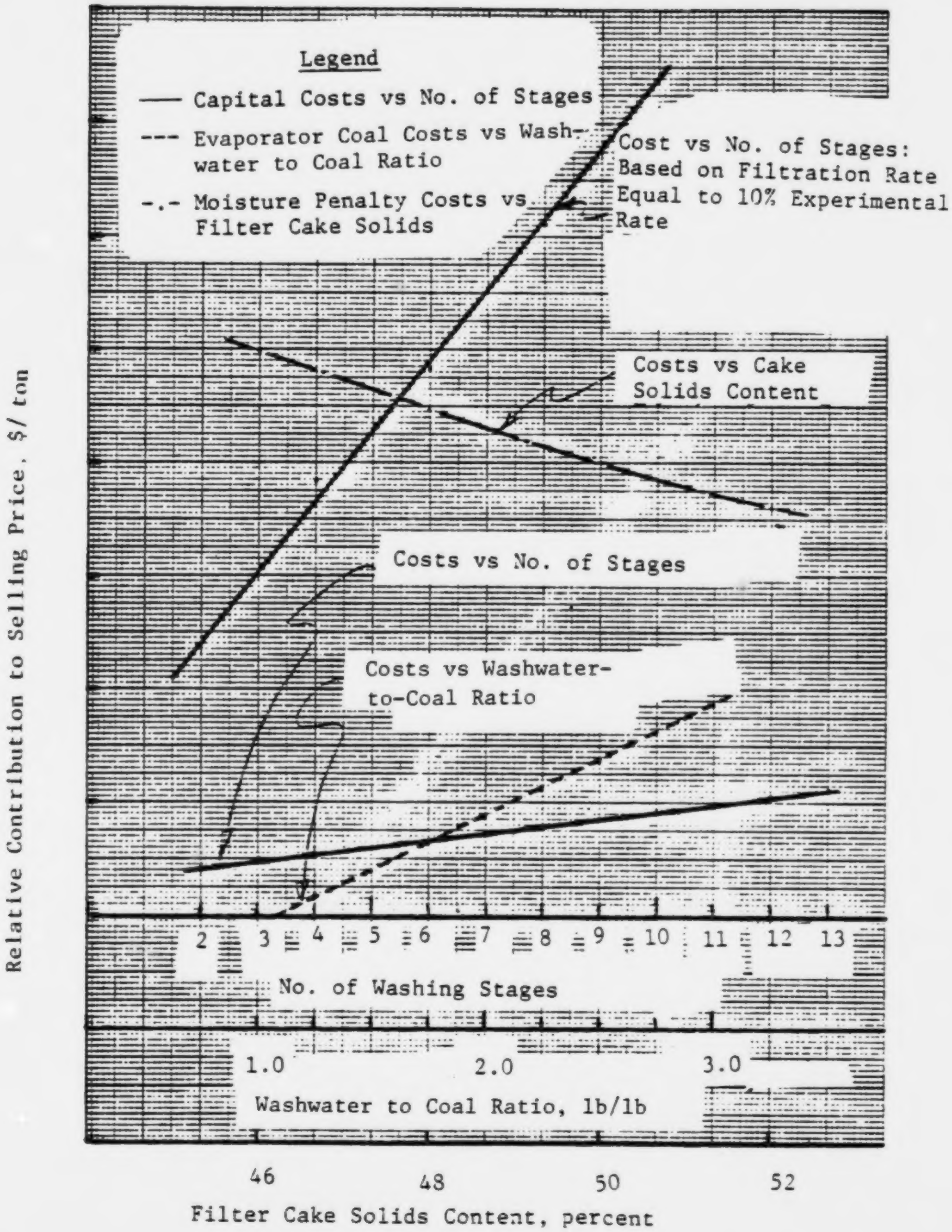

FIGURE 4. EFFECT OF PROCESS VARIABLES ON CAPITAL, EVAPORATIVE COAL AND MOISTURE PENALTY COSTS

affected by the number of washing stages but the capital cost is strongly affected by filtration rate (as noted by the upper curve); (2) the cost of treated coal for the evaporator is only moderately affected by the washwater-to-coal ratio employed; and (3) the moisture penalty is moderately affected by the filter cake solids content over the narrow range explored. This information made it clear that intensive investigation was needed to devise methods to:

- Increase the filtration rates
- Increase filter cake solid contents
- Reduce the required washwater-to-coal ratio.

It was also clear that relatively low dissolved sodium levels should be obtainable with reasonable washwater-to-coal ratios without adversely affecting the separation and washing system costs.

Experimental Procedure. An experimental test program was designed to generate the necessary separation data and to evaluate proposed improvements in the separation procedures. Knowledge of several factors was necessary to specify an optimum S/L system. Filter media type and size were the first considerations, followed by the effect of surfactant type and dosage, particle size (compressibility, temperature, pressure, and cake thickness), and oil agglomeration on the filtration rate and cake solids content.

The vacuum filtration data for this project were generated in the test apparatus depicted in Figure 5. In the original procedure, the test solution was heated to the desired temperature in an agitated, covered beaker, and charged to the 0.1 ft^2 filter leaf. A vacuum was then applied at the specified level for the length of the test. Filtrate volume as a function of time was measured along with the cake thickness and moisture content. Drying time was determined as a function of the time required to obtain a dry cake surface.

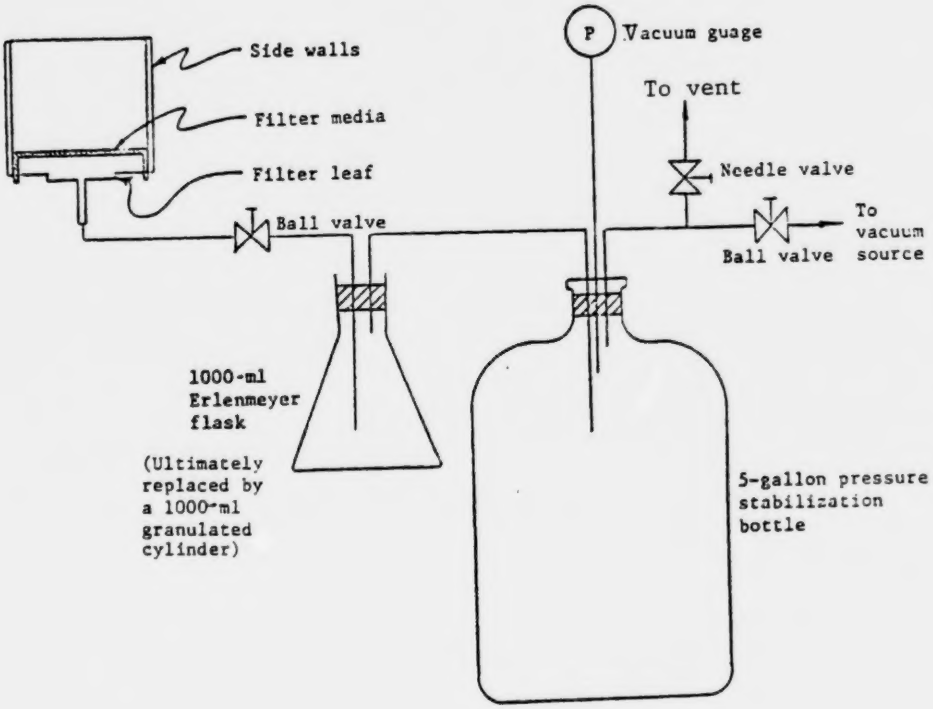
Side walls
Filter media
Filter leaf
Ball valve
P
Vacuum guage
To vent
Needle valve
Ball valve
To vacuum source
1000-ml Erlenmeyer flask
(Ultimately replaced by a 1000-ml granulated cylinder)
5-gallon pressure stabilization bottle

FIGURE 5. VACUUM FILTRATION TEST APPARATUS

This procedure was later revised by replacing the filter leaf with a specially designed adapter used to support a standard 8-in.-diameter Tyler sieve screen. Standard screens with different mesh sizes were used to provide a filter media more open than possible with the smaller filter leaf.

Simulated Solution Results. Filtration rate data were generated with a simulated HTT coal slurry. NaOH, CaO, water and coal were mixed together at ambient temperature and atmospheric pressure to make the simulated solution. Filtration tests were conducted with a -20 mesh Westland coal simulated HTT slurry prepared at NaOH/CaO/water/coal proportions of 0.16/0.05/3.0/1.0.

Clearly, the addition of very small quantities of flocculant (only RETIN 421, an anionic flocculant was tested) resulted in very significant improvements in the filtration rate and also in the dryness of the final filter cake. Also prethickening (approximately 10 min. required) of the slurry prior to filtration resulted in a further increase in the filtration rate. Rates of 1.05 to 1.92 ton/hr/ft^2 were over an order of magnitude greater than the 0.12 ton/hr/ft^2 rate used in the 1976 cost analysis. In addition, the filter cake at 20 to 30 percent moisture was much dryer than the 60 percent moisture level assumed for the 1976 economic analysis. When compared with the rates obtained with simulated solutions prepared from -200 mesh coal, there was a definite indication of a significant improvement in filtration rates and cake solids content with increased coal particle size.

HTT Solution Results. Tests were run with an actual autoclave-prepared HTT coal slurry. The coal particle size distribution is shown in Figure 6. Included in the figure are the distributions for both the -20 and -50 mesh coal samples.

The HTT coal slurry was prepared as shown in Table 4. Reactants were charged to the autoclave, heated to 535 F, held there for 14 minutes, and then cooled to about 180 F.

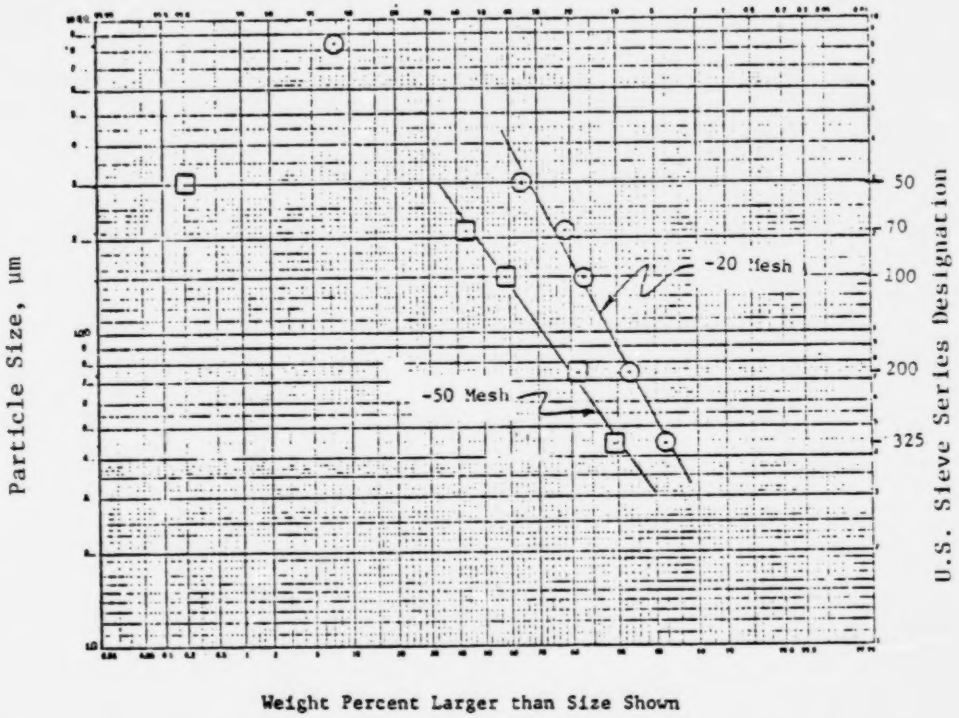

FIGURE 6. PARTICLE SIZE DISTRIBUTION OF -20 AND -50 MESH COALS

TABLE 4. PREPARATION OF HTT COAL SLURRY

Parameter	Value
Coal Type	-20 mesh Westland coal (Pittsburgh No. 3)
NaOH/Coal	0.16
CaO/Coal	0.05
H_2O/Coal	3.0
Temperature	533 F (278 C)
Pressure	993 psig
Reactor Volume	1 gal
Approximate Residence Time of Temperature	15 min

The slurry was then removed from the autoclave and transferred to a heated, agitated, nitrogen-purged beaker before being filtered.

A total of seven filtration tests were conducted with the slurry. Three different filter mediums, three filtering modes (direct filtration, prethickening and filtering, prethickening and underflow washing prior to filtration) and two flocculants (anionic and cationic) were tested. Initial experimentation revealed that the material was difficult to filter and that under normal test conditions, the filter cloth became bound within ≈30 seconds. The most successful test (Test 16) employed flocculation (cationic), prethickening, and thickener underflow washing (mixing with wash water) prior to filtration. Under these conditions (Table 5), the filtration, while slow, continued until the cake surface became dry.

Even the best filtration of autoclave-prepared HTT solution fell far below the speed and efficiency exhibited with the simulated solution. However, the addition of flocculants and prethickening resulted in an improvement over direct filtration.

In searching for an explanation for the reduced filtration rate with the real HTT coal slurry as compared to that with the simulated solution,

TABLE 5. TEST CONDITIONS FOR FILTRATION TEST 16

Parameter	Value
Filter Cloth	POPR-854 F
Slurry Temperature, F	140
Pretreatment Conditions	Flocculated (0.0001 lb/ton RETEN 205), prethickened (72 percent volume reduction) washed with 2:1 wash water/coal ratio
Filter Cake Moisture Content, percent	51.8
Filtration Rate, ton/hr/ft^2	0.03 (Separation rate without pretreatment: 0.007)
Filtrate Rate, gal/hr/ft^2	7.61

It was observed that the HTT coal slurry was composed of two distinct solid phases--a primary phase consisting of the coal product and a secondary, finely divided phase. The secondary phase appeared to be at least partially responsible for the reduced filtration rate. During filtration, a small portion of it would migrate to the filter cloth and blind it, while the major portion settled on top of the filter cake. This phase was found to contain primarily calcium, aluminum, and silicon, probably as a mixture of calcium aluminate/silicate complex salts. It is believed that the second phase is formed as the result of solubilizing the alumina and silica as soluble sodium salts which, in turn, react with the calcium to form insoluble silicate.

Quick-In/Quick-Out HTT Solution Results. In order to obtain higher filtration rates, a new slurry preparation method was explored. This procedure was designed to limit the formation of the slimey phase (responsible for the cloth blinding). The NaOH and CaO were slurried with a small quantity of water and placed into a charging cylinder while the coal and the remainder of the water were heated to reaction temperature in the autoclave. The desulfurization chemicals were then quickly charged and allowed to react with the coal for the desired residence time. The slurry was then rapidly removed from the autoclave, passed through an ice-bath-cooled, coiled-tube heat exchanger, and collected in an ice-bath-cooled autoclave. Once the temperature dropped below 212 F, the ice-bath-cooled autoclave was opened and the slurry removed to a covered, nitrogen-purged beaker where it was kept agitated at the desired filtration temperature.

Final Filtration Test Series. The quick-in/quick-out operation, which more nearly simulates commercial operation, alleviated, in part, the slime formation and, consequently, increased the filtration rate and solids content of the filter cake. However, as some blinding of the filter medium by residual slime was evident, the filter cloth was replaced with an open mesh wire screen as the filter medium. An experimental test program was employed to specify the best media, surfactant type and dosage, component compressibility, coal particle size, operating temperature and pressure, and cake thickness and effects of oil agglomeration and solvent displacement. Results are presented below.

Filter Media Effects. In tests to select the best separation media, initial experimentation with polypropylene cloth showed that the filtration rate increased as the permeability of the cloth was increased. Unfortunately, cloths with larger openings, being more rigid, were extremely difficult to install properly on the filter leaf. Therefore, tests were conducted with wire screens. An adapter was constructed to hold a standard 8-in. Tyler sieve screen. Tests showed that screens of approximately the same size as the coal worked best. The solution contacting the screen initially passed through until enough bridged over the screen to form a filtration media of collected coal particles. This technique effectively eliminated any media resistance.

Results of experiments using the new screen media for vacuum filtration showed that rates improved. However, it was observed that the rate dropped rapidly with cake thickness about 0.5 in. Therefore, a new filtration technique was employed. First the slurry was charged and allowed to form. Then the screen was tilted to allow excess slurry to drain off and the cake was allowed to vacuum dry. This technique closely simulated the actual events encountered with rotary vacuum filters. With this technique, initial separation rates were increased significantly. The best separation medium was a wire screen with a mesh size approximately the same as the coal size.

Surfactant Effects. New surfactant-aided filtration tests were conducted with the modified slurry preparation method and the modified separation technique to select the best surfactant. Four surfactants found to be beneficial in early testing were retested. The results of the tests are summarized in Table 6. Flocculants intensified the separation problem by more rapidly settling the heavier particles from the finely divided slime layer. The slime settled last and made an effective cap over the coal surface preventing the passage of filtrate through the settled coal cake. Dispersants, however, allowed the finer particles to be more evently distributed throughout the cake reducing the resistance to filtrate passage. From the test results, it appeared that the dispersant Duponal WAQE, a sodium lauryl sulfate, made the best surfactant because of its effect on filtration rate and cake solids content. As seen in Figure 7, filtration rate increased beyond a low dosage of approximately 0.5 lb/ton. Analysis of the cost of dispersant and the savings resulting from a decrease in separation stage showed an optimal dosage of 0.5 lb/ton.

Compressibility Effects. The filtration characteristics of the HTT coal solution depend on the compressibility of the slurry components. Rather than a combination of rigid, unfirom particles, the slurry is composed of a mixture of agglomerates consisting of loose assemblies of small and large particles. These agglomerates, when deposited on the cake surface, form a complicated network of flow channels. When force (either vacuum or overpressure) is exerted on the cake, the agglomerates are distorted and broken down, and their resistance to filtrate flow changes.

The traditional way to determine the degree of cake compressibility is to conduct a series of filtration tests at various constant pressures. The time filtrate volume data are then correlated by following the basic cake filtration equation.(2,3)

TABLE 6. RESULTS OF SURFACTANT AIDED FILTRATION TESTS

	Surfactant			
Test	Designation	Dosage, lb/ton	Filtration Rate with Surfactant, ton/hr/ft^2	Moisture Content, percent
43	None	0	0.008	52
56	None	0	0.009	51
50	RETIN 421 anionic flocculant	0.07	0.002	53
69	RETIN 421 anionic flocculant	0.6	0.0410	52.1
51	Tamol 850	7.1	0.004	54.8
55	Jaguar A-40-F flocculant	0.28	0.0045	54.2
67	Duponal WAQE Dispersant	0.5	0.0569	55.9
77	Duponal WAQE Dispersant	0.5	0.0808	46.5
77	Duponal WAQE Dispersant	0.75	0.0475	47.5
73	Duponal WAQE Dispersant	0.75	0.0642	52.5
76	Duponal WAQE Dispersant	0.75	0.0721	51.6
68	Duponal WAQE Dispersant	2.0	0.1026	54.0
63	Duponal WAQE Dispersant	2.0	0.1364	49.6

NOTE: Other surfactants were studied in earlier tests -- RETIN 205, a cationic flocculant; Jaguar C-13, cationic flocculant; Galactoid 210, nonanionic flocculant; RETIN 423 cationic flocculant; Galaxy XB, xanthan gum; in addition, a Celite 503 filter aid was also tested.

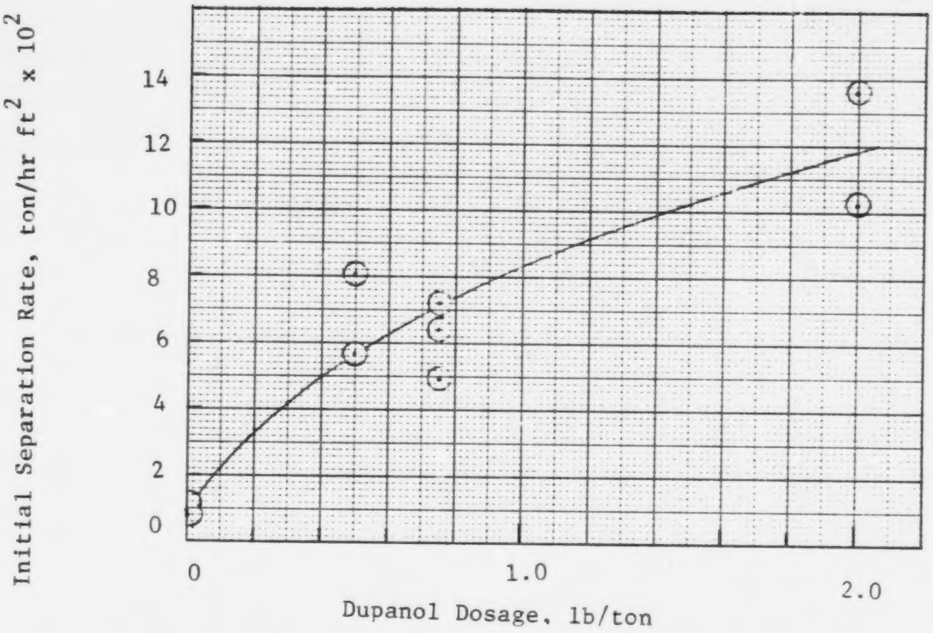

FIGURE 7. SEPARATION RATE VERSUS DISPERA'NT DOSAGE

$$\frac{dt}{dV} = K_p V + B, \text{ where } K_p = \frac{W\alpha\mu}{A^2(-\Delta P_t)g_c} \text{ and } B = \frac{R_m\mu}{A(-\Delta P_t)g_c} ,$$

where t = time

V = volume of filtrate collected

W = weight of particles deposited on the filter per unit volume of filtrate

α = specific cake resistance

μ = filtrate viscosity

A = filtration area

$-\Delta P_t$ = total pressure drop across filter media, cake, and associated piping

R_m = resistance of the filter medium and piping to filtrate flow

g_c = Newton's law proportionality factor.

Hence, a plot of $\Delta t/\Delta V$ versus V should give a straight line, of which the slope is K_p and the intercept is B. From these data, the specific cake resistance (α) and filter medium resistance, R_m, can be determined. If α is independent of ΔP the cake is incompressible; however, for most cakes α varies with $-\Delta P$. The degree of compressibility can be quantified by evaluating compressibility coefficient, S, which is related to α by the following equation:(3)

$\alpha = \alpha_o(-\Delta P)^S$, where α_o and S are empirical constants.

A limited series of experiments was conducted to evaluate α and R_m at different vacuum levels. The results of those experiments are summarized in Table 7.

TABLE 7. SPECIFIC CAKE RESISTANCE OF HTT COAL(a)

Test	Pressure Drop ($-\Delta P$), inch Hg	Specific Cake Resistance (α), ft/lb x 10^{-13}
211	10	5.83
210	15	4.51
209	20	3.80
212	27.5	2.93

(a) The medium resistance was found to be negligible.

The compressibility coefficient equation can be rearranged as follows.

$$\log \alpha = \log \alpha_o + S \log (-\Delta P).$$

Therefore, a log-log plot of the α versus $-\Delta P$ data should produce a straight line with a slope of S. The data presented in Table 7 are plotted in this fashion in Figure 8. The compressibility coefficient (S) determined from the plot in Figure 8, is -0.35, which indicates the cake is moderately compressible.

Particle Size Effects. The average particle size of the materials being filtered directly effects the rate of filtration. Large particles form a more open network of flow channels (i.e., higher porosity), allowing, in theory, more rapid removal of the filtrate. The specific cake resistance is related to the porosity, ε, by the following equation:(3)

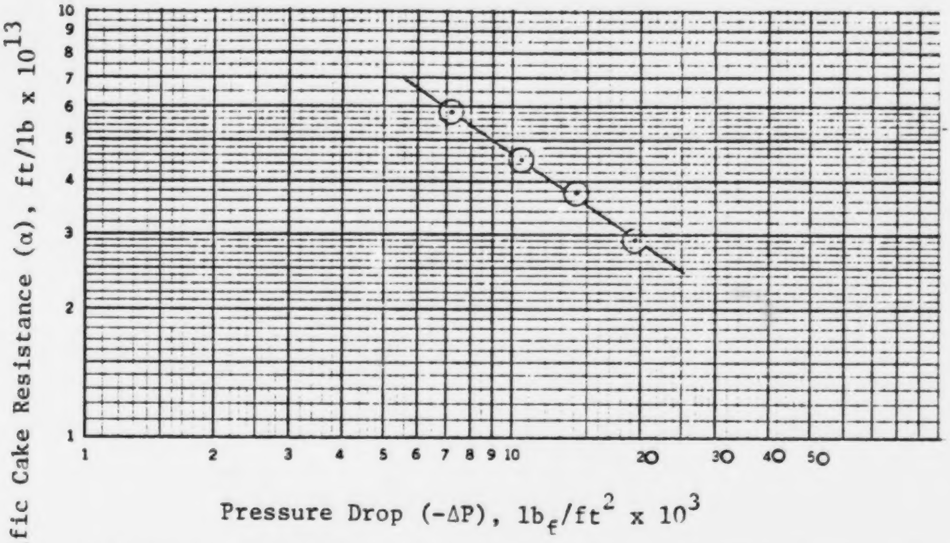

FIGURE 8. LOGARITHMIC PLOT OF SPECIFIC CAKE RESISTANCE VERSUS PRESSURE DROP TO DETERMINE THE COMPRESSIBILITY COEFFICIENT

$$\alpha = \frac{K(1 - \varepsilon)}{\varepsilon^3}$$

where K is an approximately constant factor dependent on the particle density, surface area, and volume. Thus, as the porosity increases, i.e., when larger particles are employed, the factor $(1 - \varepsilon)/\varepsilon^3$ and, thus, the specific cake resistance decrease rapidly. Since the flow rate is inversely proportional to the resistance, the flow rate will also be rapidly increased with increased cake porosity.

Test with -20, -50, and -100 mesh coal particles, after surfactant addition, showed that the rate for the larger -20 mesh coal (0.09 ton/hr ft^2) was only ≃ 15 percent higher than that for the -50 coal, but 22.5 times higher than that with the -100 mesh coal. This was not too surprising, because, over the narrow -20 to -50 mesh range, the change in porosity was not large. However, when compared to that for the -100 mesh particles, the increase in rate with the larger size particles was significant.

The optimum particle size, however, depends not only on the separation rate, but also the moisture retention characteristics and the ease of sulfur extraction and sodium washout. A comparison of these factors is presented in Table 8.

TABLE 8. PARTICLE SIZE EFFECT

	Coal Particle Size, mesh		
Factor	20 x 0	50 x 0	100 x 0
Separation rate, ton/hr ft^2	0.09	0.08	0.004
Moisture content, %	53	48	60
Sulfur extraction, % MAFs[(a)]	1.10	0.92	0.99
Sodium wash out, % Na[(b)]	0.8	0.7	0.5

(a) Treated NaOH/CaO/water/coal proportions of 0.24/0.10/1/2, at 10 minute reaction time, after one wash (comparable data for sulfur removal after a larger number of washing stages not available for all three sizes.)

(b) After seven fresh water washes at water/coal ratio of 2.0.

On the basis of all these factors, the optimum particle size was -50 mesh.

Temperature Effects. The flow of filtrate through the filter cake is governed by the general cake filtration equation for flow through a packed bed, presented in the preceding discussion on compressibility. The rearranged equation presented below states that the specific filtration rate (dV/Adt) is inversely proportional to the temperature dependent filtrate viscosity (μ).* -

$$\frac{dV}{Adt} = \frac{(-\Delta P_t)g_c}{\mu(\frac{\alpha WV}{A} + R_m)} .$$

As the temperature of the feed slurry is increased, the viscosity will decrease with a proportional increase in the filtration rate. For example, the viscosity of water (which is approximately the same as the HTT solution filtrate) decreases from 0.982 centipoises (cP) at 70 F to

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* Terms previously defined on Page 28.

0.559 cP at 120 F and down to 0.347 cP at 180 F.(4) There is little further decrease, however, as the temperature approaches 212 F. Therefore, as the filtrate temperature is increased from 70 to 180 F, the rate should increase approximately 2.8 times.

A number of experiments were conducted to establish the effect of temperature. The results are summarized in Table 9 and Figure 9. There appear to be temperature effects over and above that predicted solely from the viscosity change. The anticipated effect should show an exponential type increase, with temperature accounting for a 60 percent rate increase between 120 and 180 F where the viscosity change becomes small. The observed change, however, was a tenfold rate increase. Apparently other physical changes in the particle network, or floc structure, allowed better separation at these higher temperatures. Clearly, the higher the separation temperature, the greater the separation rate. Therefore, most separation tests were conducted at the optimum separation temperature, approximately 180 F or higher. Also note that particle size, over the narrow range studied, has little affect on the rate versus temperature relationship.

Pressure Effects. As noted in the rate equation, flow rate is directly proportional to the pressure drop. However, for compressible cakes the specific cake resistance (α) is also a function of the pressure drop. Both vacuum and pressure filtration tests were conducted to establish the effect of pressure. The results are summarized in Table 10.

The observed effect is larger than predicted (e.g., the combined effect of ΔP and α should increase the rate approximately 6 times between 27.6 and 10 inch Hg). Again, physical characteristics in this cake network allow greater separations at higher pressures. Increased pressure is beneficial as demonstrated in the vacuum filtration tests. However, with higher compressive forces in the pressure filtration tests, the solid particles deform, the flocculant aggregates break up, and the particles are forced close together, severely limiting the path for filtrate removal. At ΔP's of 20 to 40 psig on pressure filtration tests, almost no filtrate was collected even after 30 minutes. Therefore, the optimal separation system employs vacuum separation at vacuum levels of approximately 29 inch Hg.

TABLE 9. EFFECT OF TEMPERATURE ON FILTRATION RATE

Test	Raw Coal Mesh Size	Slurry Temperature, F	Filtration Rate, ton/hr/ft^2
37	-20	100	0.0032
43	-20	120	0.008
56	-20	131	0.014
59	-20	152	0.0187
76	-50	154	0.0721
73	-50	158	0.0642
99	-20	163	0.0672
78	-20	163	0.0808
60	-20	167	0.0236
114	-20	167	0.0735
108	-50	172	0.0753
115	-20	180	0.0814

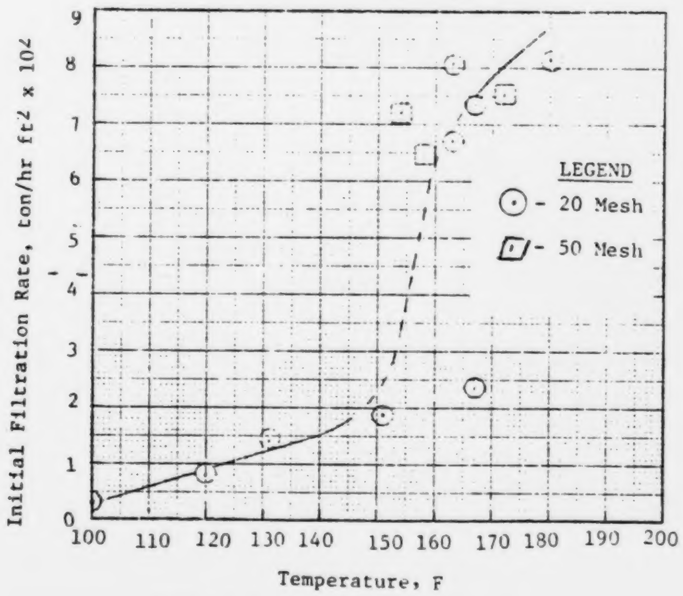

FIGURE 9. INITIAL FILTRATION RATE

TABLE 10. EFFECT OF PRESSURE DROP ON FILTRATION RATE

Test	Pressure Drop, inch Hg	Filtration Rate, ton/hr ft^2
211	10	0.004
210	15	0.008
209	20	0.019
212	27.5	0.080

Cake Thickness Effects. The filtration equation presented earlier also shows the effect of cake thickness. The terms "W · V" represent the total mass of solids in the filter cake, which can be related to cake thickness by the following equation:

$$WV = \rho_p(1-\varepsilon)AL$$

where ρ_p = density of the particle

ε = porosoty of the cake

A = filtration area

L = cake thickness.

Thus, the filtration equation can be rewritten as follows:

$$\frac{dV}{Adt} = \frac{(-\Delta P_t)g_c}{\mu(\alpha\rho_\rho(1-\varepsilon)L + R_m)} \cdot$$

Therefore, the specific filtration rate is inversely proportional to cake thickness. A number of experiments were conducted to establish the effect of cake thickness. The results are summarized in Table 11, and Figure 10. The data show that, at low cake thicknesses (<0.5 inch), the predicted effect is not observed, rather rate appears to be proportional to thickness. However, at greater thickness, the inverse relationship is noted. From the data, it is clear that the optimum thickness is approximately 0.5 inch. Also note that particle size, over the narrow range studied, has little effect on the rate-versus-cake-thickness curve.

TABLE 11. EFFECT OF CAKE THICKNESS ON FILTRATION RATE

Test	Raw Coal Size	Cake Thickness, inch	Filtration Rate, ton/hr/ft^2
62	-20	0.25	0.040
72	-50	0.28	0.044
102	-20	0.30	0.047
77	-50	0.35	0.050
74	-50	0.37	0.057
100	-20	0.38	0.079
73	-50	0.40	0.060
78	-20	0.42	0.080
74	-50	0.43	0.067
76	-50	0.45	0.072
134	-20	0.56	0.014
130	-50	0.88	0.010

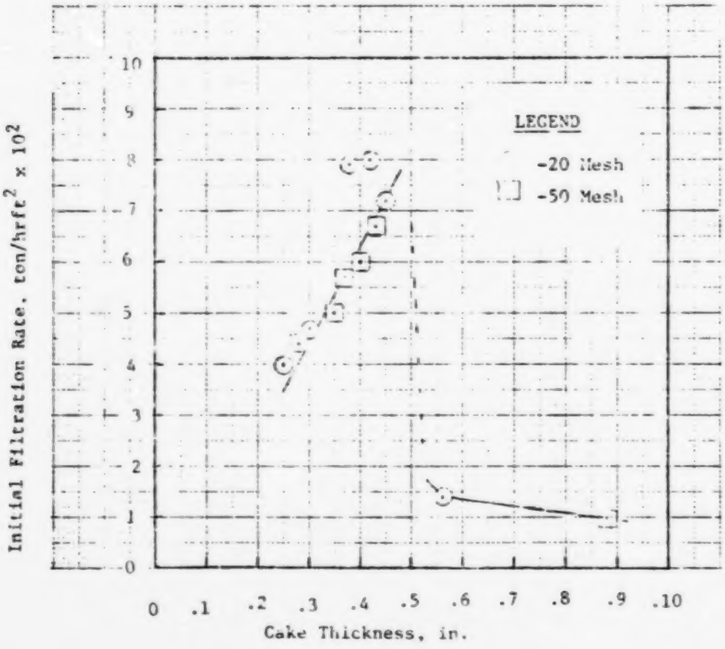

FIGURE 10. INITIAL FILTRATION RATE VERSUS CAKE THICKNESS

Oil Agglomeration Effects. One technique that has proven successful in other S/L separation processes is the use of oil to agglomerate the particles. The oil agglomeration technique can theoretically improve the filtration process by (1) making larger, more easily separated particles and (2) displacing the water from the coal particles with oil, resulting in less moisture in the product cake. Tests were conducted to evaluate this technique.

In the initial test with -50 mesh coal, the oil/water/coal slurry, containing 5 parts oil, 65 parts water, and 30 parts washed HTT coal, was mixed in a Waring blendor for 4 minutes. This action resulted in severe grinding of the coal. Consequently, the filtration rate was reduced from 0.624 ton/hr/ft^2 to 0.49 ton/hr/ft^2* which, however, was still four times higher than the rate used as the basis for the 1976 costing of the integrated process. The reduced rate (over that achievable without the addition of the oil) was the result of reduction in particle size of the coal in the Waring blender.

Tests with the larger -20 mesh coal coupled with a reduction in the blending time to 10 seconds resulted in a slurry which filtered extremely fast--equivalent to 2.2 ton/hr/ft^2. This rate, the fastest achieved in the entire program, represented an 18-fold increase over that (0.12 ton/hr/ft^2) used in the 1976 economic analysis.

The filter cake from the -20 mesh coal experiment contained 54.9 percent moisture. The higher moisture level was due to cake cracking, which prevented effective interstitial moisture removal. Lower moisture content should be achievable by preventing cracking of the filter cake.

Solvent Displacement Effects. Another technique tested for moisture removal was solvent displacement. A well-washed filter cake was used to prepare a slurry with a cake (60.5 percent moisture)/toluene/ethyl alcohol proportion of 1/1/0.5. The mixture was slurried at ambient temperature and filtered. The separated cake was found to contain 60.2 percent "moisture" (a combination of water and solvent), or approximately the same as the starting cake. During the moisture determination, it was noted that it took almost exactly half the energy to remove the "moisture" from the solvent-washed cake. Therefore, it appears that the solvent effectively displaced much of the water as planned, but that the solvent was not subsequently removed during the separation step as hoped. It is possible that other techniques, such as mechanical expression, could produce a substantially lower moisture final filter cake.

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* Note that these high rates were obtained on washed HTT coal which separates at a significantly higher rate than the raw slurry exiting the autoclave reactor.

Centrifugal Separation

Centrifugation evaluations were designed to determine the effects of various process variables on the cake moisture content. The test equipment was considered too small to generate accurate rate data; therefore, the rate was based on information from the Bird Machine Company. The problem was first studied through a computerized simulation model to determine those variables with the greatest influence on processing costs. The theoretical study was followed by a 300 lb/hr experimental program with a 6-inch-screen, bowl centrifuge. The study included both separation and washing tests.

Theoretical Economic Considerations. The simulation model allowed the indentificcation and effective investigation of the most important varialbes. Cake solids content followed by unbound sodium level and washwater-to-coal ratio had the greatest influence on processing costs. From data shown in Figure 11, it was clear that centrifugal separation was considerably more expensive than vacuum filtration (but less expensive than thickening) for equal cake moisture contents. Only when the centrifuge produced cakes dryer than 38 percent moisture did it become competitive.

The obvious solution was a combined filter-centrifuge system. The initial separation and washing was conducted using filtration separation, followed in the final stage by centrifugal separation. A modified simulation model was constructed to study this option. The result showed that the combined system was more economical than either the filtration or centrifugal separation route. (More cost details are presented later.) Experiments were,

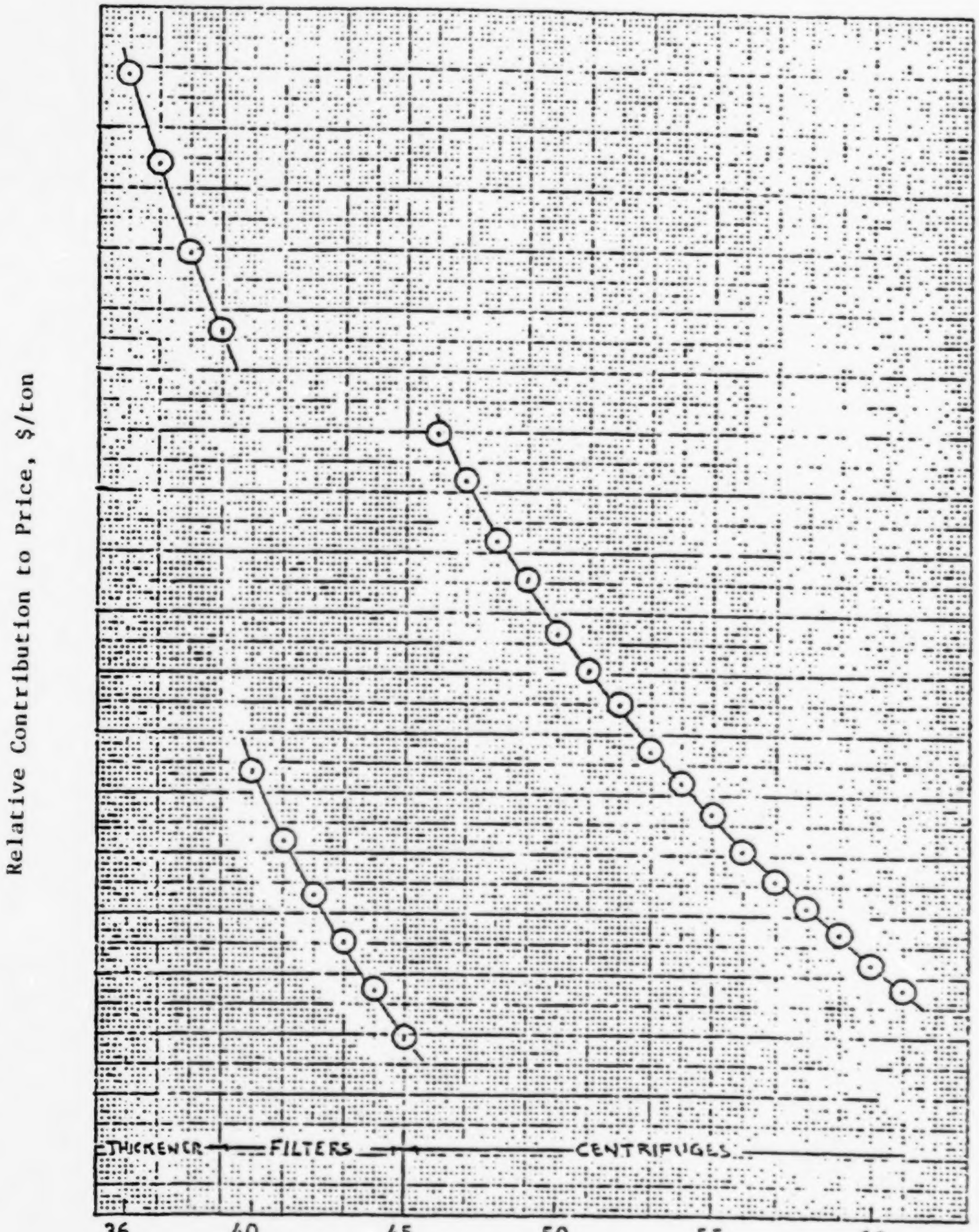


FIGURE 11. S/L SEPARATION COSTS VERSUS SOLIDS UNDERFLOW

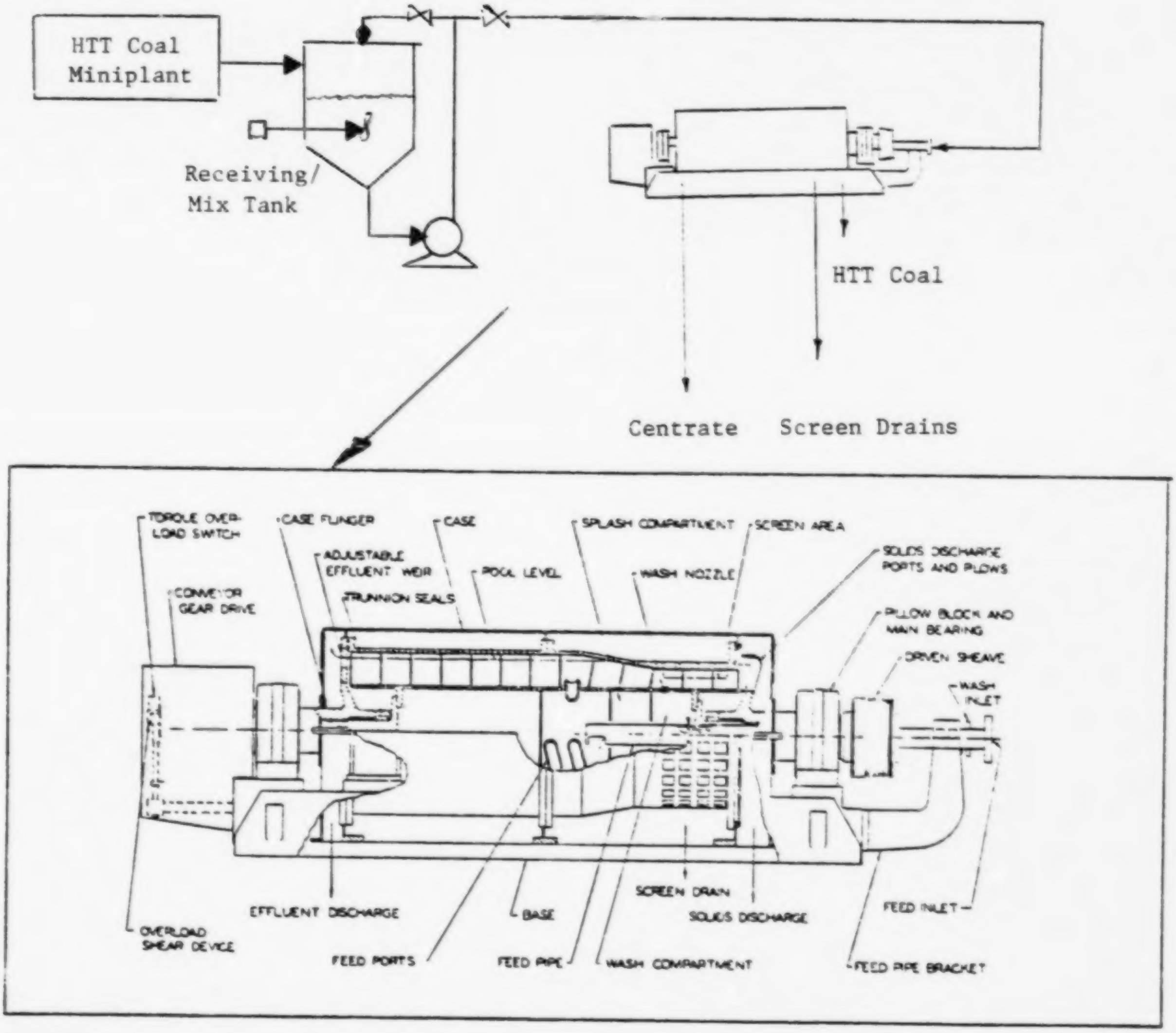
therefore, conducted to determine the minimum cake moisture content achievable by centrifugation.

Experimental Procedures. An experimental test program was designed to generate the necessary design data to evaluate proposed improvements in the separation and washing system. The study included investigation of the effects of variable feed solids content and separation rates on moisture content. Tasks were conducted with centrifuge washing, repulp washing, and repulp washing with surfactant additions and with oil agglomeration.

The centrifugation data were generated in the test setup depicted in Figure 12. The HTT coal slurry was generated in Battelle's HTT miniplant, collected in a 100-gal feed tank, and fed to a Bird 6-inch screen, bowl centrifuge. The centrate, screen drains, and product cake were collected for analysis. The unit was not equipped for variable speed, so all tests were conducted at a constant 561 gravities.

Separation Rate. No attempt was made to generate rate data because of the small size of the equipment. Rates for design purposes were estimated by the Bird Machine Company based on equipment employed in coal processing applications with similarly sized coal particles. The largest unit should provide separation rates of approximately 50 gons of dry solids/hr. In addition, from extensive laboratory and field studies, Bird has established that the moisture content of the centrifuge cake varies in direct proportion to the -325 weight fraction. Therefore, the use of -50 (11 percent -325 mesh) rather than -100 (60 percent -325 mesh) coal particles should theroretically drop the moisture content of the product cake by at least 15 to 20 percent. Because no accurate rate data were obtainable in these experiments, the main emphasis of all the centrifuge experiments was on cake moisture content.

Simulated Solution Results. As in the filtration test, the first test was conducted with a simulated HTT solution of -20 mesh coal and water. The test was conducted with a familiar material to set the machine to the proper pool depth and select the best screen drain opening size. In three tests, the centrifuge cake ranged from 11.9 to 14.2 percent moisture. As


HTT Coal Miniplant
Receiving/ Mix Tank
HTT Coal
Centrate
Screen Drains
TORQUE OVER-LOAD SWITCH
CASE FLINGER
CASE
SPLASH COMPARTMENT
SCREEN AREA
ADJUSTABLE EFFLUENT WEIR
POOL LEVEL
WASH NOZZLE
SOLIDS DISCHARGE PORTS AND PLOWS
CONVEYOR GEAR DRIVE
TRUNNION SEALS
PILLOW BLOCK AND MAIN BEARING
DRIVEN SHEAVE
WASH INLET
SCREEN DRAIN
EFFLUENT DISCHARGE
BASE
SOLIDS DISCHARGE
FEED INLET
OVERLOAD SHEAR DEVICE
FEED PORTS
FEED PIPE
WASH COMPARTMENT
FEED PIPE BRACKET

Expanded View of Centrifuge

FIGURE 12. SCREEN-BOWL CENTRIFUGATION TEST APPARATUS

in the filtration tests, the results with the simulated solution were much better than those obtained with the actual HTT coal solution.

HTT Solution Results. Seven tests were conducted with the screen bowl centrifuge; three separation tests and four washing tests. The results are summarized in Table 12. In the separation tests, the effect of the feed solids concentrate and separation rate were studied. Higher concentrations appeared to decrease the moisture content (from 42 to 40.3 percent), while higher rates appeared to increase it (from 42 to 42.3 percent). However, in no case did the moisture content vary much from 42 percent. These tests showed that centrifugal separation offers a significant improvement in cake moisture content over filtration separation.

Combined Washing and Separation. Tests conducted on the centrifuge (i.e., wash water sprayed through the wash nozzles during separation) were not successful in terms of practical applicability. At wash rates approaching the necessary 1-2 lb/ton rate, the cake became quite wet. Test 4, conducted with only a 0.10 lb/ton wash ratio, produced a cake with approximately the same moisture content as the unwashed cake, but removed little of the residual sodium. In Tests 5, 6, and 7, the separated cake was mixed thoroughly with washwater and fed to the centrifuge. In Test 6, Duponal (a sodium lauryl sulfate dispersant) was added and in Test 7 the slurry (of once-washed coal) was oil agglomerated prior to separation. As noted in the table, neither the addition of dispersant nor oil improved the moisture content of the product cake. In both cases, the moisture content was 42.4 percent or approximately the same as in the unwashed HTT coal. Thus, centrifugal separation can (1) provide a relatively dry final product cake, ≈ 42 percent moisture, and (2) produce a cake relatively insensitive to the number of washing stages. (This is in contrast to repulp washing followed by filtration separation where the product cake typically increases in moisture 0.5 to 1.0 percent per wash.)

Material Balance. The inlet and outlet mass flow rates for screen-bowl centrifuge Test 6, which employed dispersant with a washed HTT coal slurry, are summarized in Figure 13. A mass and solids balance for Test 6

TABLE 12. SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS CENTRIFUGE TESTING WITH HTT COAL SLURRY

Test[(a)]	1	2	3	4	5	6	7
Test Time, min	3.5	3.0	5.0	4.0	--	26.5	
Feed:							
Moisture content, %	71.7	71.4	63.6	65.2	75.0	81.1	85.6
Wet rate, lb/hr	375.4	731.1	388.5	455.0	--	336.9	
Dry rate, lb/hr	106.3	209.2	141.1	158.1	--	63.5	89.5
Volumetric rate (wet), gpm	0.59	1.14	0.57	0.66	0.75	0.62	1.16
Temperature, F	149	149	149	149	100	84	104
Sp gravity	1.28	1.28	1.374	1.374	ND(b)	1.088	1.074
Cake:							
Moisture content, %	42.0	42.3	40.3	40.2	42.4	42.4	43.2
Wet rate, lb/hr	120.8	250.7	170.9	179.7	ND	97.7	143.1
Dry rate, lb/hr	70.1	144.6	102.1	107.4	ND	56.2	81.3
Centrate:							
Moisture content, %	90.7	90.3	88.0	87.0	--	98.5	99.0
Wet rate, lb/hr	213.6	410.5	170.9	136.9	ND	225.3	465.0
Dry rate, lb/hr	19.8	39.9	20.5	17.9	ND	3.3	4.7
Screen Drains:							
Moisture content, %	61.2	64.4	59.7	76.3	--	71.4	75.4
Wet rate, lb/hr	41.7	69.9	46.5	138.7(c)	ND	13.9	15.0
Dry rate, lb/hr	16.1	24.9	18.7	32.8	ND	4.0	3.7
Recovery,(d)	81.3(e)	81.0	85.5	88.8	ND	94.6	94.9
Wash:							
Method				On-centrifuge	Repulp	Repulp	Repulp
Solids history				Fresh slurry	Cake	Rewashed Cake	Rewashed Cake
H_2O/dry solids, lb/ton				0.10	3.0	3.0	3.0
Additive				None	None	SLS(f)	0.1(g)

(a) Centrifuge operating conditions common for all tests: 2596 rpm, 561 gravities, 100/1 slip/gear ratio, 1.1 cm pool depth, 0.1 to 0.03 cm screen drain openings with circumferential slots.

(b) ND = Not determined

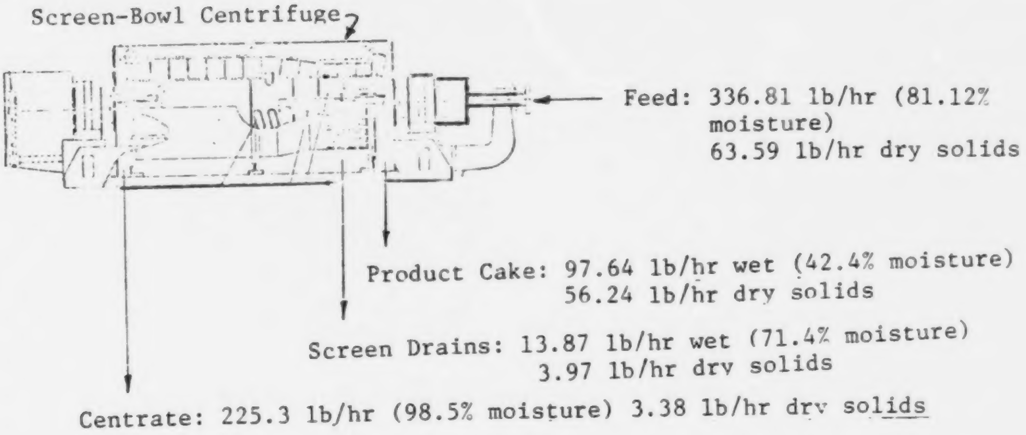
(c) Includes wash water

(d) Recovery = weight of cake plus screen drains/weight of solids fed

(e) This recovery suspect because of material b-lance problems

(f) SLS - technical grade sodium lauryl sulfate

(g) Slurry oil agglomerated with oil (combination of Nos. 4, 5, and 6) at 0.035 lb/lb dry coal dosage



Feed: 336.81 lb/hr (81.12% moisture)
63.59 lb/hr dry solids

Product Cake: 97.64 lb/hr wet (42.4% moisture)
56.24 lb/hr dry solids

Screen Drains: 13.87 lb/hr wet (71.4% moisture)
3.97 lb/hr dry solids

Centrate: 225.3 lb/hr (98.5% moisture) 3.38 lb/hr dry solids

FIGURE 13. SCREEN-BOWL CENTRIFUGE TEST 6

TABLE 13A. MASS AND SOLIDS MATERIAL BALANCE FOR CENTRIFUGE TEST 6

Mass Balance: In = 336.81 lb/hr; Out = 97.64 + 13.87 + 225.3 = 336.81 lb/hr

Solids Balance: In = 336.81 lb/hr x (1 - 0.8112) = 63.59 lb/hr dry solids

Out = 97.64 lb/hr x (1 - 0.424) = 56.24 lb/hr dry product cake solids +

13.87 lb/hr (1 - 0.714) = 3.97 lb/hr dry screen drain solids +

225.3 lb/hr (1 - 0.985) = 3.38 lb/hr dry centrate solids = 63.59 lb/hr dry solids

Solids Recovery: $\left(\frac{\text{56.24 lb/hr dry cake + 3.97 lb/hr dry screen drains}}{\text{63.59 lb/hr total dry solids}}\right) \times$

100 = 94.68%

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and solids recovery are summarized in Table 13. The Test 6 results showed that nearly 95 percent of all feed solids (coal, lime, and caustic) were recovered in the cake or screen drains, from which materials are returned to the centrifuge feed tank. This recovery figure was improved significantly by the addition of dispersant. Tests without the sodium lauryl sulfate dispersant had recoveries of 81 to 89 percent. The addition apparently was beneficial in the reduction of fine solids collected in the centrate. With dispersant, the centrate percent solid dropped from ≈ 11 percent to only 1.5 percent. While the dispersant had no noticeable effect on cake moisture content (still approximately 42 percent), it improved centrate clarity and solids recovery. Therefore, because the cake moisture content was still above 38 percent (the moisture level established by the cost simulation model as the dividing point between an economically superior all-filter or all-centrifuge system), the all-centrifuge route remained economically unattractive. However, the results appeared favorable for a combined filter centrifuge system. In a combined system, the filter would effectively remove the sodium from the washed cake, while the centrifuge would lower the final moisture content of the product cake. In addition, the dispersant added with the initial filtration step should be available in the final centrifuge stage to improve centrate clarity and solids recovery.

TABLE 13B. DISPLACEMENT WASHING TESTS FOR WESTLAND COAL[(a)]

Step	Filtration Rate, ton/hr/ft^2	Cake Moisture Content, wt %	Dissolved Sodium Content, wt %
Initial separation	0.0045	51	2.82
First wash	0.0029	52	1.68
Second wash	0.0039	53	1.04
Third wash	0.0055	54	0.65
Fourth wash	0.0059	55	0.40
Fifth wash	0.0069	56	0.22

(a) HTT treatment with NaOH/CaO/H_2O/coal proportions of 0.24/0.10/3/1, with -50 mesh coal. Filtration conducted with 50 mesh screen filter media at 180 F and 29 inch Hg vacuum without surfactant addition. Wash water/coal ratio equaled 1.0 for each wash.

Washing

The S/L separation section of the BHCP was designed to separate (1) the coal solids from the treated coal slurry and (2) the valuable sodium compounds from the separated HTT coal. Previous testing showed that the coal could be separated from the slurry, but at a relatively low rate and with high residual sodium levels. Therefore, any commercially acceptable process would require washing to remove the sodium. Two washing methods were considered in this project: displacement and repulp washing. Experimental evaluations of both methods were conducted. Tests were also conducted to evaluate the effects of initial $NaOH/CaO/H_2O$ coal ratings, washing media additives, and washing time.

Displacement Washing. Experimental testing conducted in 1976 and 1977 indicated that displacement washing was impractical based primarily on the very low separation rates obtained. However, because of the excellent potential for efficient, low-water-requirement washing that existed, new displacement washing tests were conducted. Results of these tests are summarized in Table 14. At this low separation rate, washing would require 483, 1200 ft^2 belt filters costing over $130 million. Assuming that, with the use of surfactants, the initial rate could be increased to a level comparable to that obtained in the repulp wash experiments (0.08 $ton/hr/ft^2$) and that similar improvements in rate would be obtained as the coal was washed, the estimated cost of the S/L separation section alone was over $18/ton. This price was far in excess of that estimated for the repulp option and herefore, further work on displacement washing was abandoned.

Repulp Washing. Once the basic separation problem had been examined, the test program moved to cake washing to determine the effect of number of washes on filtration rate, cake moisture and sodium extraction from the cleaned coal. Repulp washing was employed because of experimental evidence that it was superior to displacement washing. Using repulp washing at a water to coal ratio of 1, a series of tests was conducted to establish the effect of coal particle size and reaction time on the separation rate

TABLE 15. RESULTS OF SILTRATION EXPERIMENTS WITH -20 AND -50 MESH HYDROTHERMALLY TREATED WESTLAND COAL

	Filtration Rate (ton/hr/ft^2)		Moisture Content (percent)		Sodium Content (Moisture free percent)	
	tr = 10 min	tr - 30 min	tr = 10	tr = 30	tr = 10	tr = 30
	20 Mesh Feed Coal					
Initial Filtration	0.104(a)/0.085(b)	0.081(c)	53.3(a)/53.3(b)	52.5(c)	4.42(a)/4.59(b)	4.54(c)
First Wash	0.189/0.083	0.092	54.2/52.8	43.2	2.91/3.06	2.92
Second Wash	0.166/0.253	0.355	55.2/53.4	54.0	2.12/2.60	2.45
Third Wash	0.169/0.836	0.384	53.5/54.5	56.9	1.71/2.17	2.01
Fourth Wash	0.594	2.196(f)	51.8	54.9(f)	1.47	1.78(f)
	50 Mesh Feed Coal					
Initial Filtration	0.081(d)	0.075(e)	49.5(e)	47.7(e)	4.53(d)	3.84(e)
First Wash	0.364	0.099	48.2	49.6	3.09	2.61
Second Wash	0.340	0.332	49.3	50.5	2.48	2.19
Third Wash	0.310	0.624	50.2	51.9	2.23	1.87
Fourth Wash	0.590	0.4880(f)	51.5	59.1(f)	1.81	1.55(f)

(a) Test Nos. 89-94
(b) Test No. 83-88
(c) Test Nos. 114-119
(d) Test Nos. 77-82
(e) Test Nos. 108-113
(f) Oil agglomeration treatment prior to filtration.

Ref. October 31, 1977 Monthly Report Input.

* tr--residence time

and residual dissolved sodium level. The results of these tests are summarized in Table 15. A number of conclusions were drawn from these data.

Effect on Separation Rate. Investigation of separation rate led to the following conclusions.

- Surfactant -- the use of the dispersant Duponol WAQE resulted in an approximately tenfold increase in the separation rate (see Table 8)
- Particle size -- for both -20 and -50 mesh Westland coal, the initial separation rate was ≈ 0.08 ton/hr/ft^2 (with dispersant), which appears unaffected by treatment time. The rate did not appear significantly affected by particle size in this narrow range but was increased significantly with -100 mesh coal.
- Washing -- the separation rate increased significantly with the degree of washing. Although the rate of increase was not constant in each experiment, overall, the increase averaged 50 to 100 percent per washing stage. The rate increased until eventually reaching approximately 0.6 ton/hr/ft^2 after four washes; little further increase was noted.
- Oil Agglomeration -- oil agglomeration increased the rate of separation significantly - equivalent to 2.2 ton/hr/ft^2.
- Reaction Time -- reaction time apparently had little effect on separation rate.

Effect on Moisture Content. The following conclusions relate to experimental results on moisture content of the separated coal.

- Surfactant -- without the use of the surfactant Dupanol, the cake moisture content of the unwashed coal ranged from 52 to 59 percent for -20 mesh feed coal. With dispersants, the moisture content ranged from 52 to 53 percent for the -20 mesh coal and 48 to 50 percent for the -50 mesh coal.

- Particle size -- the -50 mesh HTT coal retained 3 to 5 percent less moisture per corresponding stage of washing as compared to the -20 mesh coal. In contrast, the smaller -100 mesh retained 10 to 12 percent more than the -50 mesh coal. Thus, use of larger sized raw coal improved the moisture retention problem.
- Washing -- the cake moisture content was a direct function of the degree of washing, it increased 0.5 to 1.0 percent per washing stage for the -20 mesh coal and ≈1.0 percent per stage for the -50 mesh coal.
- Reaction time -- reaction time apparently had little effect on the cake's final moisture content.
- Oil Agglomeration -- the moisture content of the oil-treated coal was dependent on the degree of mixing. Extensive blending increased the moisture content by 3 to 5 percent (to 59 percent); light mixing resulted in little or no improvement.

Effect on Sodium Removal. The following conclusions were drawn regarding sodium removal.

- Washing -- the residual sodium level was an exponential decay function of the number of washing stages. Starting at 4.5 percent (MF), the sodium level dropped slowly to below 2 percent after four washes. This level, far above acceptable sodium levels, indicated that new treatment techniques or more extensive washing was required.
- Particle size -- the particle size, in the narrow range, had little effect on final sodium levels. The effect was pronounced, however, when compared to -100 mesh treated coal.
- Reaction time -- reaction time apparently had little effect on the final sodium levels.
- Oil agglomeration -- the use of oil had no noticeable adverse or beneficial effect on the washing operations sodium removal efficiency.

Effects of Improved Repulp Washing. As evidenced by the results summarized in Table 15, the sodium was not removed from the HTT coal to the desired levels. Several hypotheses for the high sodium retention are:

1. The calcium oxide could contain calcium carbonate, which is ineffective in replacing the sodium.
2. The coal could be oxidized and, therefore, more susceptible to sodium retention.
3. The coarser sized coal (-20 and -50 versus -100 mesh experimented with in earlier studies) allowed sodium to penetrate into the interior of the particles where it was effectively washed out.
4. The quantity of calcium in the slurry was not sufficient to displace the sodium in the coal matrix, thereby resulting in excessively high residual sodium levels, i.e., the calcium reacted with the ash rather than with the sodium in the coal.

The first hypothesis was tested using a freshly opened bottle of chemical grade lime, but this did not result in significant sodium reduction. Testing of the second hypothesis did not give the results expected. No significant reduction in the sodium content (through the second wash) of the HTT coal was achieved by using freshly ground coal in place of coal which had been exposed to the atmosphere for several days or weeks after grinding. Other factors may also be responsible for the high sodium retention; for example, the sodium hydroxide concentrations and calcium hydroxide in the slurry. In the early 1977-78 experimentation, the coal was treated at NaOH/CaO/H_2O/coal proportions of 0.16/0.05/2/1. Thus, the sodium hydroxide concentration was only 5.3 weight percent. In pre-1977 work, the sodium hydroxide concentration was maintained within the range of 6 to 10 weight percent. In addition, a relatively low CaO/coal ratio (0.05) was employed. For some coals, higher CaO/coal ratios were required to effectively reduce the residual sodium levels of the HTT coal to the desired 0.5 percent or less. Therefore, experiments were conducted at higher sodium hydroxide and calcium oxide concentrations to test the third and fourth hypotheses.

Three series of washing tests were conducted with NaOH/CaO/H_2O/coal proportions of 0.24/0.10/2.0/1 employing coal ground to -20, -50, and -100 mesh. The ground coal was treated in the laboratory autoclave and then washed by repulping with hot, fresh water at a 2/1 water/dry coal ratio. The results are presented in Figure 14.

Three conclusions were drawn from these tests. First, the additional reaction chemical did not sifnificantly increase the reduction of sodium in the washed cake when equal volumes of washwater were used. Second, the total sodium content of the coal could be reduced to approximately 0.5 percent sodium (the bound sodium level), but only after 12 washes for the larger sized coal particles. Third, the sodium in the -100 mesh treated coal particles washed out to the greatest extent when an equal volume of washwater was used. However, because of the improved filtration rates possible with the larger coal particles, other specialized washing techniques were developed.

Special Repulp Washing Tests. Three new washing techniques were tried in an attempt to remove sodium more efficiently: (1) saturated -CO_2-water wash, (2) extended mix-time wash, and (3) saturated lime-water wash. The results of these tests, along with a standard wash for comparative purposes, are presented in Figure 15. Clearly, the saturated lime-water wash was superior. Not only was the dissolved sodium removed more efficiently (in a fewer number of washes), but the total sodium was removed to a significantly lower level (meaning that some previously bound sodium was also extracted). Because of the improved washing efficiency and the fact that lime-water wash (saturated lime water contains less than 0.1 percent calcium by weight) would add very little to total processing costs, lime water washing was chosen for use in the final washing circuit.

In order to evaluate the effectiveness of these washing techniques, the sodium equilibrium between filtrate and filter cake was compared with the theoretical value. Although the lime water wash comes closest to the theoretical curve, the difference between actual and theoretical is still significant. A comparison of the theoretical versus actual sodium contents of washed cakes is presented in Table 16.

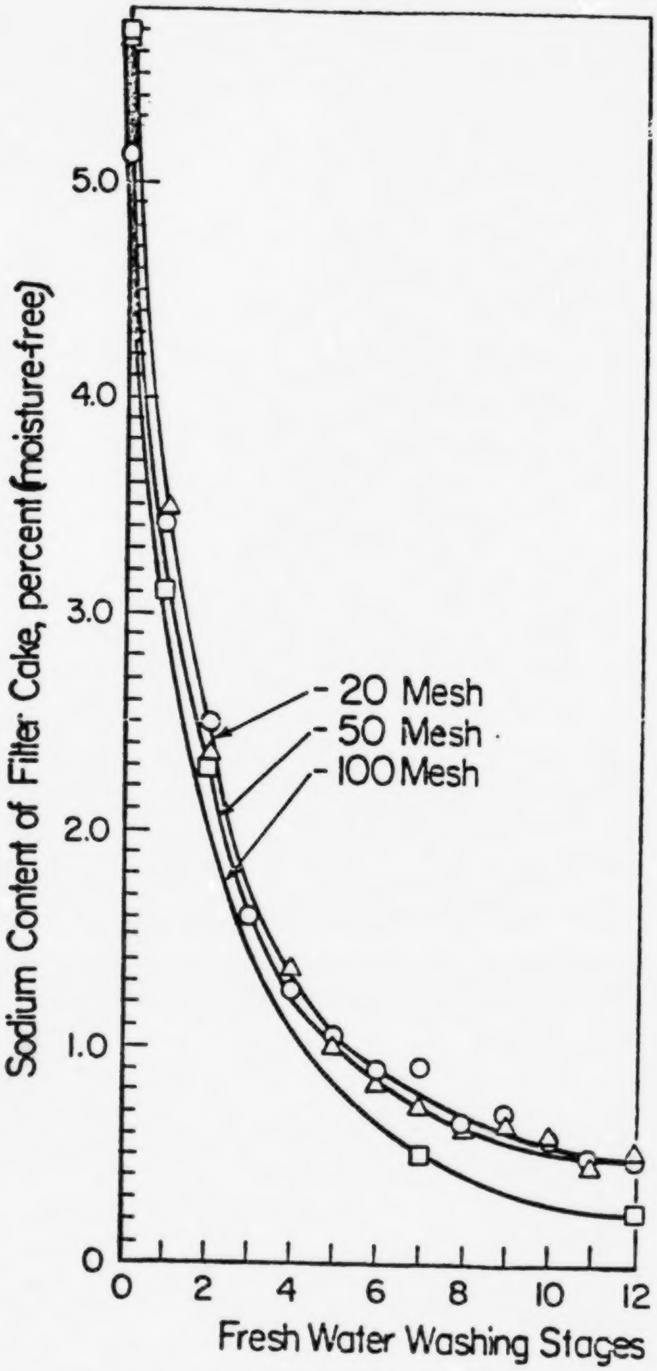

FIGURE 14. SODIUM REMOVAL VERSUS NUMBER OF WASHING STAGES AS A FUNCTION OF STARTING COAL PARTICLE SIZE

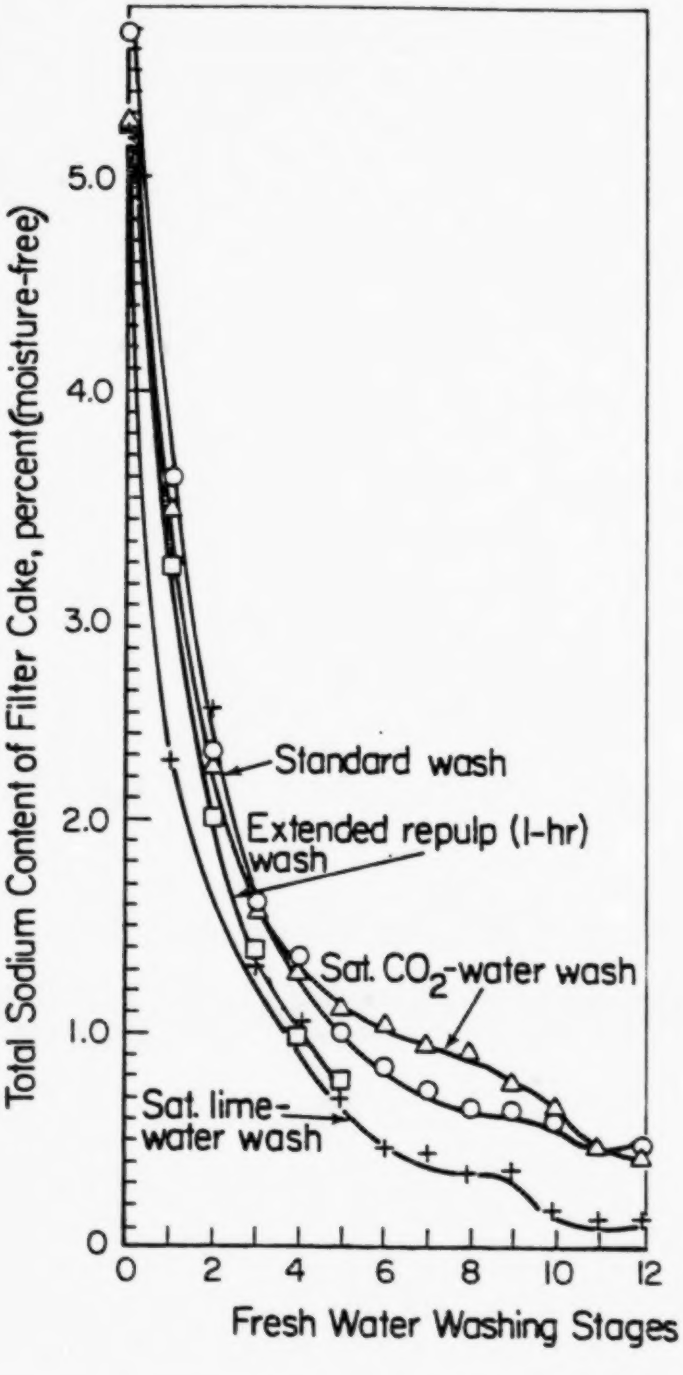

FIGURE 15. SODIUM REMOVAL VERSUS NUMBER OF WASHING STAGES FOR -50 MESH HTT COAL AS A FUNCTION OF SPECIAL WASHING METHODS

TABLE 16. COMPARISON OF THEORETICAL AND ACTUAL SODIUM CONTENT OF WASHED HTT COAL FILTER CAKE AS A FUNCTION OF THE NUMBER OF WASHING STAGES(a)

Washing Stage	Theoretical Sodium Content (with 0.1% bound sodium) of HTT Coal lb sodium/lb dry solids	Actual Sodium Content of Lime Water Washed HTT Coal, lb sodium/ lb dry solids(c)
1	0.0192	0.0333
2	0.0067(d)	0.025
3	0.0034(e)	0.0129
4	0.0019(f)	0.0105
5		0.0069(d)
6		0.0046
7		0.0043
8		0.0035(e)
9		0.0033
10		0.0017(f)
11		0.0013
12	0.0010	0.0010

(a) Washwater/dry coal ratio - 2.0. Fresh water used for each repulp wash.

(b) Based on perfect mixing between solids and liquids and no removal of ash, sulfur, or coal solids with filtrate.

(c) Lime water repulp washing using 2.0/1.0 saturated lime water/dry coal for each wash.

(d) Two theoretical washes are approximately equivalent to five actual washes, 40 percent stage efficiency.

(e) Three theoretical washes are approximately equivalent to eight actual washes, 38 percent stage efficiency.

(f) Four theoretical washes are approximately equivalent to ten actual washes, 40 percent stage efficiency.

From the table, a stage efficiency of about 40 percent is apparent, i.e., it requires 10 actual stages to wash out the amount of sodium that would be removed with four theoretical stages. (This stage efficiency was used to correct the computer model of counter-current decantation washing allowed for the selection of the optimal washing circuit.)

Sulfur and Ash Removal Tests. While the increased reactant chemical concentrations did not notably improve sodium removal, the use of a higher NaOH concentration (0.24 lb NaOH/lb coal versus 0.16 lb NaOH/lb coal) resulted in more complete removal of sulfur and ash. Before increasing the sodium concentration, sulfur content of 1.0 percent (MAF) or greater were not unusual. With the additional caustic, sulfur levels were consistently below the current 1.2 lb/10^6 Btu NSPS levels, equivalent to 0.9 percent (MAF) sulfur for 15,000 Btu/lb (MAF) coal. By employing higher CaO concentrations (0.10 lb/lb versus 0.05 lb/lb) in the leaching solution, the percentage of CaO (MF) retained with the filter cakes naturally rose. The calcium was partially removed during washing along with the ash to produce a final HTT coal which was relatively low in ash. With the lime water wash of -50 mesh coal, the initial filter cake's ash content was reduced from 22 percent (MF) to 8 percent (MF) after five washes. This compares favorably with the raw Westland coal which had an ash content of 7.9 percent (MF).

Material Balance Tests. An experiment was conducted to obtain material balance data for the washing circuit. Unlike the true counter-current washing method proposed, in these experiments fresh water rather than filtrate was used to wash the cake. A schematic of the washing liquid separation circuit, employing vacuum filtration separation, is presented in Figure 16. The hydrothermally treated slurry was first mixed with surfactant and separated. The cake was then mixed with hot washwater and separated again. The cake went on to the next washing operation while the filtrate was collected, settled, and the settleable solids recycled to the washing operation. Use of large open mesh screens as the filtering media allowed some particles to pass through the filter prior to the filter cake build up. These solids

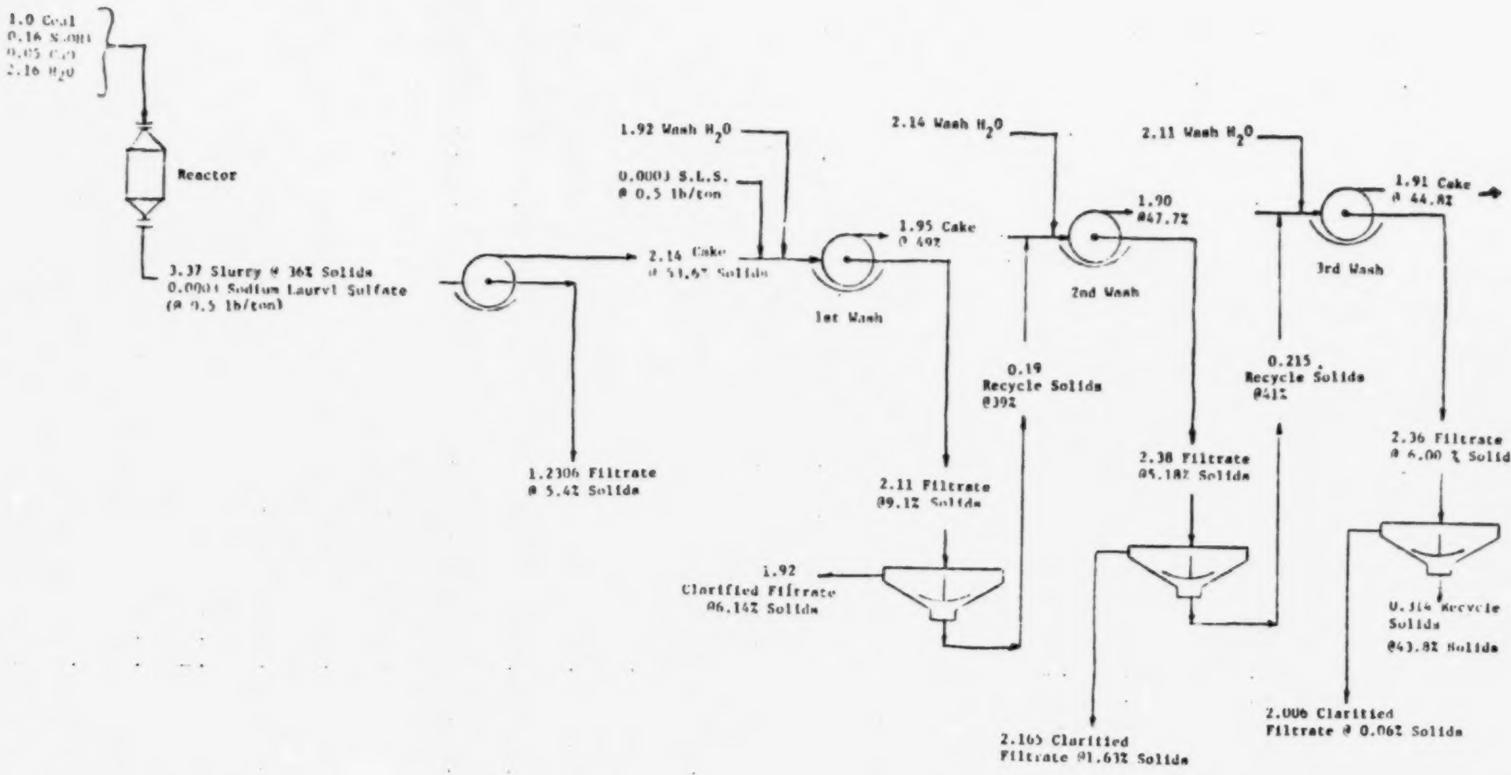
1.0 Coal
0.16 NaOH
0.05 CaO
2.16 H_2O
Reactor
3.37 Slurry @ 36% Solids
0.0004 Sodium Lauryl Sulfate
(@ 0.5 lb/ton)
1.2306 Filtrate
@ 5.4% Solids
1.92 Wash H_2O
0.0003 S.L.S.
@ 0.5 lb/ton
2.14 Cake
@ 51.6% Solids
1st Wash
1.95 Cake
@ 49%
2.11 Filtrate
@9.1% Solids
1.92
Clarified Filtrate
@6.14% Solids
0.19
Recycle Solids
@39%
2.14 Wash H_2O
1.90
@47.7%
2nd Wash
2.38 Filtrate
@5.18% Solids
2.165 Clarified
Filtrate @1.63% Solids
0.215
Recycle Solids
@41%
2.11 Wash H_2O
1.91 Cake
@ 44.8%
3rd Wash
2.36 Filtrate
@ 6.00 % Solids
0.314 Recycle
Solids
@43.8% Solids
2.006 Clarified
Filtrate @ 0.06% Solids

FIGURE 16. SOLID/LIQUID SEPARATION - WASHING CIRCUIT MATERIAL BALANCE SCHEMATIC

were not lost, however, but simply collected and recycled.

The following four conclusions can be drawn from the material balance diagram.

1. The moisture content of the filter cake increased slightly with each separation and washing.
2. The amount of nonsettleable solids progressively decreased with each washing stage, which resulted in improved thickener overflow clarity.
3. The quantity of solids recoverable by thickening the filtrate increased with each washing stage.
4. The moisture content of the thickener underflow decreased with each washing step.

LEACHANT REGENERATION AND COAL DESULFURIZATION

Background

"Spent" aqueous caustic soda leachant (utilized in the Battelle Hydrothermal Coal Process to remove sulfur and other constituents from coal) contains the sulfur, primarily in sulfide form, that has been extracted from the coal. The work discussed in this section, was concerned with developing an improved method for regenerating this spent leachant, i.e., removing sulfur, so the leachant could be recycled to the process.

When coal is desulfurized with aqueous sodium hydroxide, inorganic sulfur and, to some degree, organic sulfur are solubilized. Since the major portion of the solubilized sulfur is from pyrite, the primary reaction, which produces sulfide sulfur, is believed to be as follows:

$$2FeS_2 + 8NaOH + \begin{array}{c}\text{oxidized}\\ \text{coal}\\ \text{species}\end{array} \longrightarrow 4Na_2S + Fe_2O_3 + \begin{array}{c}\text{reduced}\\ \text{coal}\\ \text{species}\end{array}$$

Another possible reaction, involving oxidation of part of the sulfur is:

$$FeS_2 + NaOH + \begin{array}{c}\text{oxidized}\\ \text{coal or } O_2\\ \text{species}\end{array} \longrightarrow Na_2S + Na_xS_yO_z + Fe_2O_3 + \begin{array}{c}\text{reduced}\\ \text{coal}\\ \text{species}\end{array}$$

where

S_yO_z represents $S_2O_3^{--}$, SO_3^{--}, and/or SO_4^{--}.

As is indicated, the oxidizing agent can be oxidized coal species or oxygen introduced by exposure of the solution to air.

Previous work at Battelle on the recycle of the sodium hydroxide leachant solution had shown that the desulfurizing effectiveness of the leachant decreased as the concentration of sulfide sulfur in the solution sulfur in the solution increased. The results (see Figure 17) indicated, however, that acceptable desulfurization could be obtained with sulfide concentrations as high as about 0.13 percent (~1.43 g/ℓ).

Comprehensive review and exploration of sulfur chemistry have revealed only effective desulfurization reactions that involve sulfide sulfur forms. These reactions were of two types: (1) evolution of sulfide in the gas phase as hydrogen sulfide, and (2) the precipitation of insoluble sulfides.

Thus, there were two requirements for the leachant desulfurization process:

- Retention of reacted sulfur in the sulfide state by avoiding oxidation
- Decrease residual sulfide concentration in the regenerated leachant to a low level.

Previous work on the Battelle Hydrothermal Coal Process included extensive investigation of the carbon dioxide-lime process for leachant regeneration. In this process, the leachant solution is treated with carbon dioxide, producing the following neutralization reaction:

$$2NaOH + 2CO_2 \longrightarrow 2NaHCO_3 \ .$$

When the pH becomes low enough, one of two desulfurization reactions occur:

$$Na_2S + 2CO_2 + 2H_2O \longrightarrow H_2S \uparrow + 2NaHCO_3$$

or

$$NaSH + CO_2 + H_2O \longrightarrow H_2S \uparrow + NaHCO_3 .$$

The evolved hydrogen sulfide is treated by the Claus process to produce sulfur and the leachant is re-causticized by treatment with lime:

$$NaHCO_3 + CaO \longrightarrow \underline{CaCO_3} + NaOH.$$

The precipitated calcium carbonate then is calcined to reclaim the carbon dioxide and lime for recycle:

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow \ .$$

The carbon dioxide-lime process has the advantages of straightforward recycle of required materials and of yielding sulfur in a form that can be converted to the elemental form by a standard process. Disadvantages are the higher-than-desired cost and the poor kinetics of the carbonation step.

In this effort on regeneration of the spent leachant several criteria had to be met for the approach to be technically feasible: (1) separation of the sulfide sulfur from the spent leachant, (2) recovery of the regeneration material for recycle, and (3) essentially complete separation of the regeneration material to avoid contamination of the coal. With these criteria in mind, several candidate systems as discussed below were selected for study. Zinc and copper systems were selected for study because these materials are known to form sulfides readily in alkaline systems and the resulting sulfides can be thermally decomposed to recover the materials for recycle. Previous work had demonstrated the specific iron compound would separate the sulfide sulfur from the spent leachant. Also, residual iron would not contaminate the coal. Activated carbon, if successful, could be regenerated thermally and would not contaminate the coal. Via electrolysis, elemental sulfur, in theory, can be produced directly from sulfide solutions.

APPROACH

The major approach to the regeneration of leachant was concerned with the use of metallic oxides to remove the sulfide from the spent leachant. Two oxides were studied--iron oxide and zinc oxide. A screening study was conducted to select the more effective of these two and then the best system was refined to develop a near-optimum set of processing conditions for removing the sulfide sulfur and regenerating the metallic sulfide for recycle.

The metallic oxides do not remove the extracted trace metals. Therefore, build up of impurities such as trace metals and solubilized coal, in the regenerated leachant could progressively decrease desulfurization efficiency and contaminate the product coal as the regenerated leachant is recycled. In order to evaluate this effect, a series of recycle experiments were conducted to determine how many times the regenerated leachant can be recycled and whether or not a bleed stream is needed to prevent contamination of the coal product.

Also, metallic oxides do not remove the oxidized forms--thiosulfate, sulfite, and sulfate--of sulfur from the spent leachant. These oxidized sulfur forms, which are known to be detrimental to desulfurization of coal, are believed to be produced during the desulfurization process and/or upon exposure of the spent leachant to the atmospheric oxygen. As part of this subtask, efforts were directed toward controlling these oxidized sulfur forms. Several approaches were studied:

1. Maintaining the spent leachant prepared as discussed in Appendix 3.B under a nonoxidizing atmosphere at all times.
2. Reduction of the oxidized sulfur with, for example, metals such as iron and/or zinc and gaseous hydrogen during the regeneration of the spent leachant and/or during the desulfurization operation.

Finally, the results of these various studies were integrated into the overall Hydrothermal Coal Process and an economic analysis was conducted.

Summary

The candidates initially investigated for regeneration of the spent leachant were:

1. Zinc compounds--zinc oxide and sodium zincate
2. Iron compounds such as $Fe(OH)_2$, $Fe(OH)_3$, reduced/activated iron oxide, $Fe_2O_3 \cdot H_2O$, $FeO(OH) \cdot Fe_3O_4$, elemental iron, hematite, iron carbonyl, water soluble iron compounds--sodium ferrite iron nitrate, and iron carbonate
3. Activated carbon
4. Electrolysis
5. Lime
6. Copper.

Of the systems evaluated, zinc oxide, $Fe(OH)_{2-3}$, reduced activated Fe_2O_3, and iron carbonate were effective in removing essentially all or a major portion of the sulfide sulfur from the spent leachant. The results are summarized below.

Zinc Oxide

Complete removal of sulfide sulfur from the spent leachant was achieved with zinc oxide, depending on the ZnO/S ratio and temperature. At 80 C and ZnO/S ratios of 3 and 1.75, 100 percent removal was achieved in 10 and 30 minutes, respectively. At a ratio of 1.25, approximately 85 percent was removed in 60 minutes. At 40 C and a ZnO/S ratio of 3, 98 percent was precipitated in 60 minutes at 40 C.

Potential problems associated with the use of zinc oxide are: (1) residual zinc in the regenerated leachant, which might contaminate the coal product upon recycle of the leachant and (2) regeneration of the zinc sulfide for recycle. Total sulfide sulfur removal from the spent leachant for recycle is not necessary. Previous work at Battelle has demonstrated that regenerated leachants from hydrothermal treatment of other coals containing about 0.1 percent sulfide sulfur can be recycled without any adverse effect on the degree of desulfurization. Therefore, this problem can probably be minimized by removing the majority of the sulfide sulfur without solubilizing an appreciable amount of the zinc.

Because of the cost of zinc oxide, the zinc sulfide from regeneration of the leachant must be regenerated for recycle. This is achieved commercially by roasting under oxidizing conditions. The zinc sulfide reacts with the oxygen to form zinc oxide and sulfur oxides. The sulfur oxides are converted to sulfuric acid, whereas the zinc oxide is mixed with a reducing agent, generally carbon, and reduced to metallic zinc. Originally, it was contempleted that direct roasting would produce a zinc oxide for recycle. However, after further consideration and discussion with zinc producers, it is considered doubtful that a zinc oxide of the desired particle size can be produced by this approach. Therefore, it may be necessary to roast the zinc sulfide to zinc oxide, reduce the zinc oxide to metallic zinc, and then oxidize the zinc metal to zinc oxide by the American process.

Conclusions drawn from the screening studies on the zinc oxide system were that sulfide sulfur can be removed from the spent leachant as zinc sulfide with this system. However, complete removal of the sulfide sulfur results in a regenerated leachant containing soluble zinc. Since complete removal of the sulfide sulfur is not necessary for recycle of the leachant, zinc concentration in the regenerated leachant might be reduced to an acceptable level by leaving a small concentration of the sulfide sulfur in the leachant, thereby reducing the potential for contamination of the coal upon recycle of the regenerated leachant.

Iron Compounds

Certain iron compounds are candidates for regeneration of the spent leachant. Freshly prepared $Fe(OH)_3$ was the most effective. At an $Fe(OH)_3/S$ ratio of 3, 90 to 98 percent of the sulfide sulfur was removed at about 25 C in 60 minutes. $Fe(OH)_2$ gave a sulfide sulfur removal efficiency of about 80 percent under the same conditions. When properly prepared, iron oxide that had been reduced with hydrogen and then partially oxidized (reduced activated Fe_2O_3) was effective in removing 80 to 90 percent of the sulfide sulfur. Other iron compounds, such as untreated Fe_2O_3, Fe_3O_4, FeO, metallic iron and soluble iron compounds did not remove the sulfide sulfur from the spent leachant.

Regeneration of the iron sulfides from reaction of the reduced activated Fe_2O_3 with hydrogen appeared to be technically feasible. Treatment of leachant with once-generated oxide resulted in the removal of about 85 percent of the sulfide sulfur; twice-regenerated oxide removed about 80 percent of the sulfur. The lower degree of sulfur removal may have resulted from a lower Fe/S ratio--8 as compared to 11.

Freshly precipitated iron carbonate was found to be an effective agent for the desulfurization of the spent leachant. At $FeCO_3/S$ ratios of 1.5 to 10, sulfide sulfur extractions of 80 to 97 percent were obtained with 30-minute treatment times at room temperature. With an FeCO3/S ratio of 1.5, adequate desulfurization for recycle of leachant--80 to 83 percent sulfide removal and 76 percent total sulfur extraction--was obtained.

A method was devised and checked for recycle of the iron values as iron carbonate. This involved: (1) separating the precipitated iron sulfide from the leachant, (2) dissolving the iron sulfide with sulfuric acid solution, and (3) precipitating the iron as carbonate by use of sodium carbonate.

A regeneration process outlined for evaluation was based on the use of iron carbonate and recycle of the iron values as just discussed.

Conclusions drawn from the iron carbonate studies were:

- Freshly precipitated iron carbonate is an effective leachant desulfurizing agent when used in proportions as low as 1.5 times the stoichiometric proportion.
- The sulfide concentration in spent leachant can be reduced well below the acceptable level for satisfactory recycle.
- The iron values can be recycled to the leachant regeneration loop by the sulfuric acid-sodium carbonate method.

Other Methods of Regeneration

Other leachant regeneration approaches involving electrolysis and the use of activated carbon, soluble iron compounds, lime, and copper were investigated and were found to be unsatisfactory for various reasons.

Coal Desulfurization Studies

Near-optimum hydrothermal desulfurization treatment conditions were identified for three representative coals to demonstrate the applicability of the hydrothermal process for treating a variety of coals. Near-optimum processing conditions are as follows:

Northern Appalachian Coal (Homer City Coal)

Leachant -- NaOH-CaO
  H_2O/coal ratio -- 3
  NaOH/coal ratio -- 0.26
  CaO/coal ratio -- 0.10
Temperature -- 275°C
Time -- 10 minutes

Western Coal (Colstrip Mine)

Leachant -- H_2O
  H_2O/coal ratio -- 3
Temperature -- 275°C
Time -- 10 minutes

Midwestern Coal (Illinois No. 6)

Leachant -- NaOH - CaO
  H_2O/coal ratio -- 3
  NaOH/coal ratio -- 0.26
  CaO/coal ratio -- 0.10
Temperature -- 275°C
Time -- 10 minutes

Under these conditions, a clean solid fuel with a sulfur content less than the 1971 sulfur emission standards for new sources was produced from the Northern Appalachian and Western coals. That produced from the Midwestern coal would not meet this standard. However, the alkali (calcium) left in the coal will act as a sulfur getter during combustion. Therefore, based on prior work at Battelle, it should be possible to burn the cleaned coal from treatment of the Midwestern coal as well as the cleaned coals from the other coals with little or no sulfur emission.

Results and Discussion

Leachant Regeneration with Zinc Compounds

Analytical results indicate that sulfur is extracted from coal with the mixed leachant system--a mixture of sodium hydroxide and lime--as sulfide sulfur, providing the leaching operation is conducted in the absence of oxygen. It is possible that oxidized forms of sulfur--thiosulfate ($S_2O_3^{=}$), sulfite ($SO_3^{=}$), and/or sulfate ($SO_4^{=}$)--are produced as intermediates, but are reduced to sulfide sulfur by the reducing action of any ore or a combination of

- The coal and/or reducing gases formed by the action of the alkali
- Heat
- Water on the coal.

The sulfide sulfur can be removed from the spent leachant by precipitation as zinc sulfide through the following reaction:

$$S^{=} + Zn^{++} \qquad ZnS\downarrow$$

When zinc ions are added to the spent leachant, the sulfur present as sulfide sulfur should precipitate as zinc sulfide. Sulfur in the form of thiosulfate, sulfite, and sulfate will not be precipitated. In order to minimize the effect of unwanted anions, the zinc sources employed were the oxides, ZnO, and the zincate ion, $ZnO_2^{=}$, added as the sodium salt. Anticipated reactions were:

$$ZnO_{(s)} + S^{=}(aq) + H_2O = ZnS_{(s)} \downarrow + 2OH^{-}$$

$$ZnO^{=}_{2(aq)} + S^{=}_{(aq)} + 2H_2O = ZnS_{(s)} \downarrow + 4OH^{-}.$$

Alternative approaches considered for the regeneration of the spent leachant with zinc were:

- Contact the leachant with ZnO as a powder of high-surface-area pellets (fixed bed), then add sodium hydroxide to adjust alkali deficiency.
- Treat with a solution of Na_2ZnO_2 in excess sodium hydroxide. The concentration of sodium hydroxide used would be determined by the amount of NaOH needed to bring the regenerated leachant to the final concentration of 2M NaOH. Enough ZnO would be dissolved in this NaOH solution to react with the sulfide ion.
- Treat leachant with a fixed concentration of Na_2ZnO_2 in NaOH, then adjust alkali value by dilution or addition of NaOH (Solid or solution).

In the last of these approaches, metallic zinc might serve a twofold purpose: (1) precipitate the sulfide and (2) reduce oxidized sulfur species, if present, to sulfide. The metallic zinc might be added along with the ZnO. (See Appendix 3.C for experimental procedures.)

Areas of uncertainty were the characteristics of the ZnS precipitate formed from these reactants at various temperatures and with various methods of mixing. Precipitation of ZnS from solution produces a finely divided, difficult-to-filter solid. There also is a tendency for colloidal dispersions to form when the zinc ion is complexed, as is the case with zincate solutions where the zinc species exist principally as $Zn(OH)_4^{=}$. The use of high-surface-area ZnO powders or pellets to provide a substrate on which ZnS could form might overcome the separation problem.

Incremental addition of soluble sodium zincate (Figure 18) over a period of 60 minutes resulted in the removal of 94 percent of the sulfide sulfur. A ZnO/S mole ratio of 0.78 was almost as effective as ratios of 0.9 and 1.0. The addition of all the soluble zinc oxide at one time, in an amount equivalent to a Zn/S ratio of 1, (Figure 19), was not as effective as incremental addition. The reduced sulfide removal efficiency may have resulted from coating

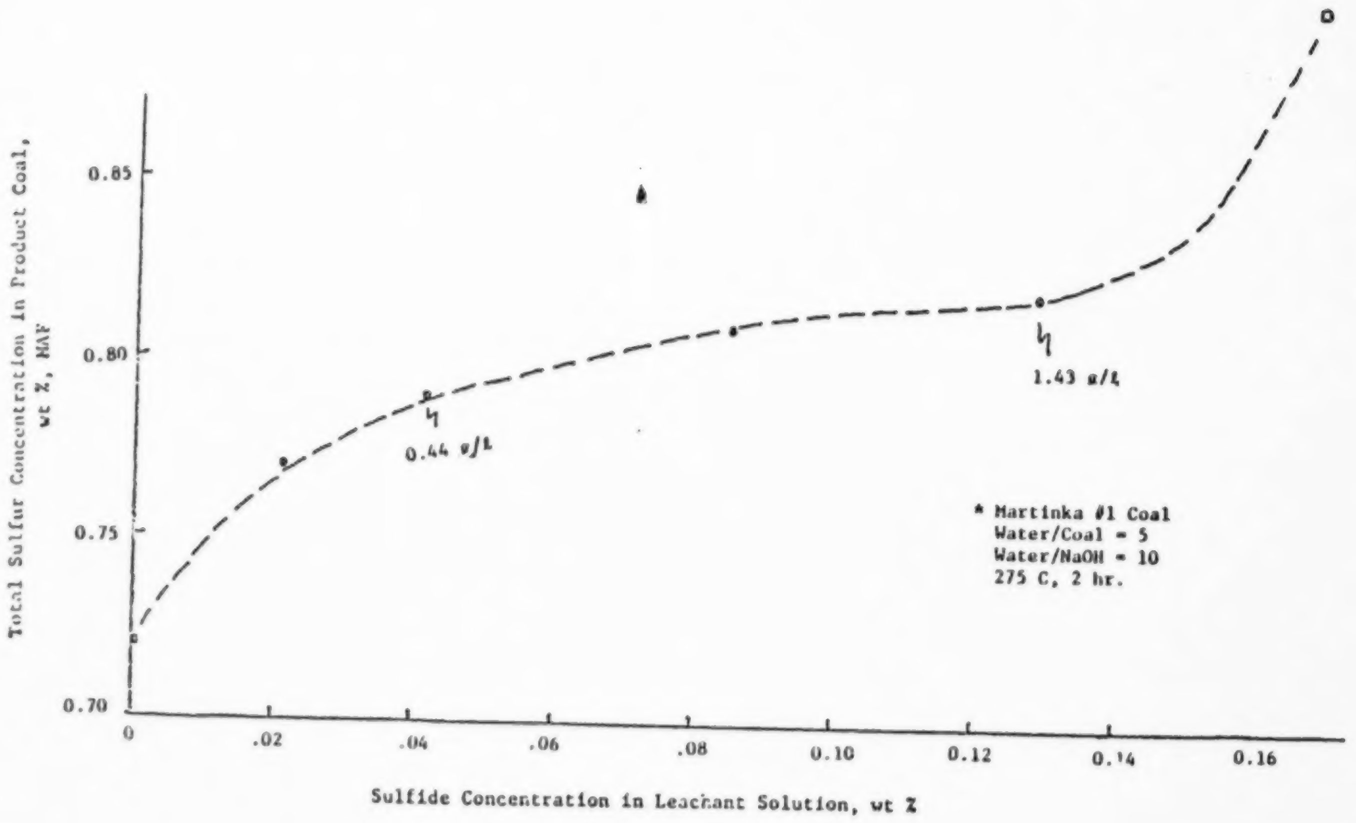

FIGURE 17. SULFUR CONCENTRATION IN HTT COAL VERSUS SULFIDE CONCENTRATION IN LEACHANT

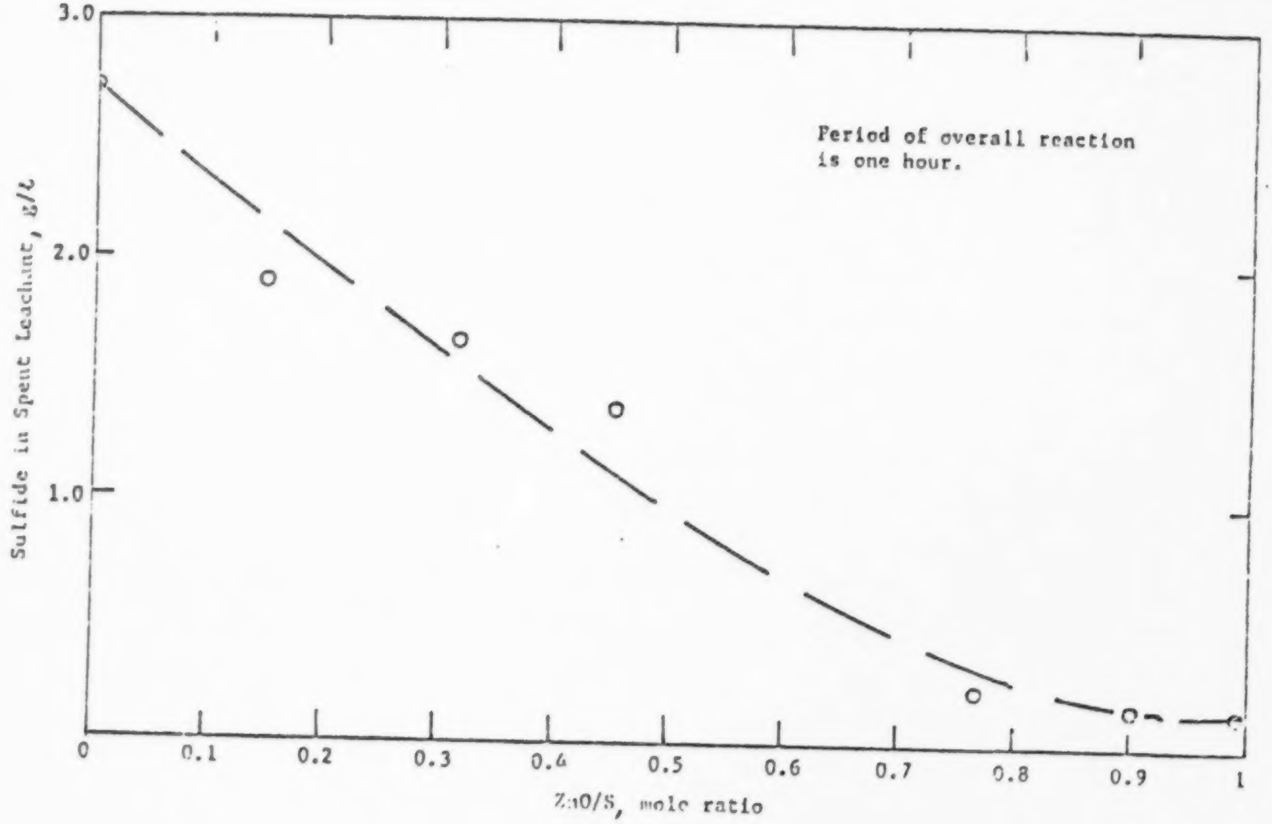

FIGURE 18. DESULFURIZATION OF SPENT LEACHANT BY INCREMENTAL ADDITION OF SODIUM ZINCATE

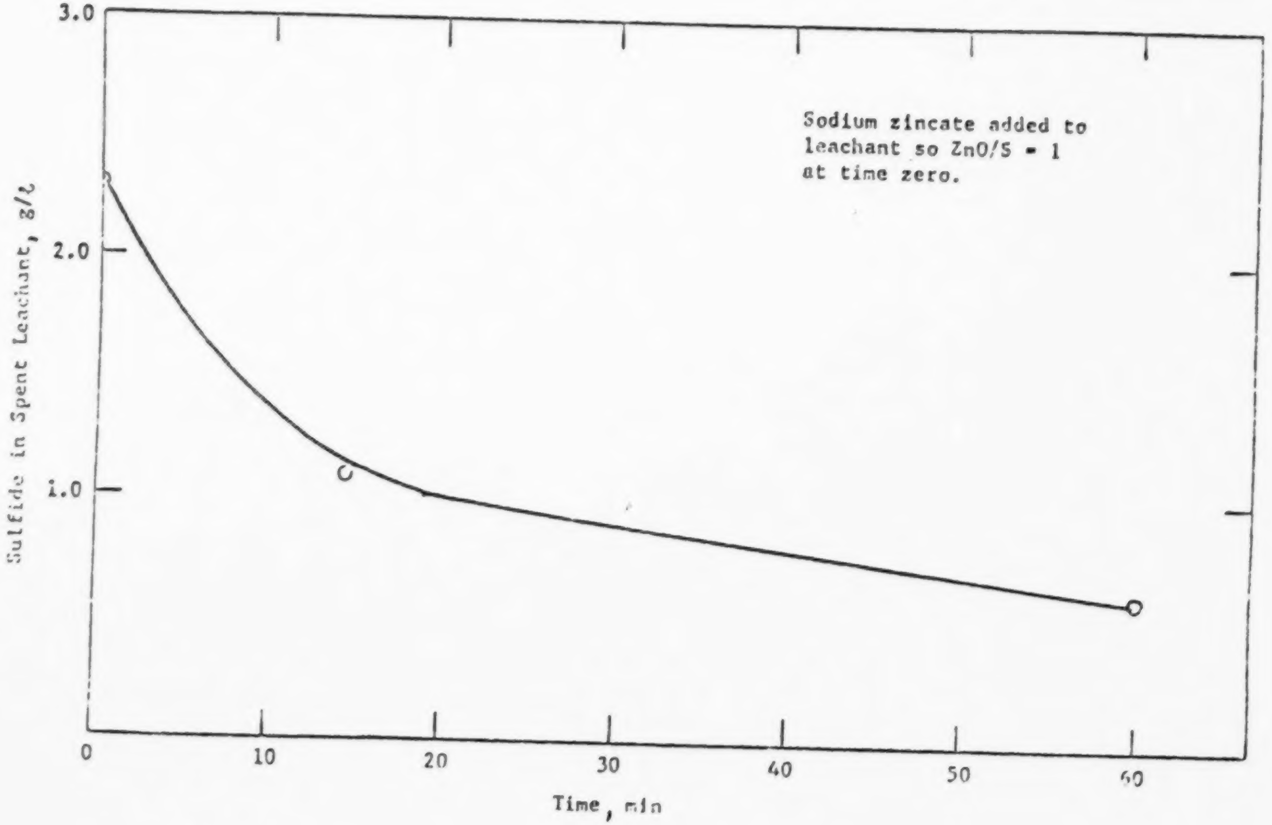

FIGURE 19. DESULFURIZATION OF SPENT LEACHANT WITH SODIUM ZINCATE AS A FUNCTION OF TIME (ANALYSES INCOMPLETE)

of the $Zn(OH)_4^=$ with ZnS, which prevented the sulfide sulfur from coming in contact with the zinc.

The results of a series of experiments performed in a batch reactor system at 80 and 40 C are shown in Figure 20. At 80 C, and a ZnO/S ratio of 3, complete sulfide removal was achieved in 10 minutes. As the ZnO/S ratio was decreased to 1.75, complete removal occurred in about 30 minutes and no apparent dissolution of sulfide ion occurred after an hour of exposure. At a ratio of 1.25, approximately 85 percent was removed in about 15 minutes. Allowing the slurry to digest for another 45 minutes resulted in the removal of an additional 9 percent, raising the overall removal to 94 percent in 60 minutes. Reducing the ZnO/S ratio to 1.0 resulted in the removal of 73 percent of the sulfur in 60 minutes, of which 69 percent was removed in the first 10 minutes. This is the same level (73 percent) attained when sodium zincate was added batchwise at a Zn/S ratio of 1. (However, the lower rate of removal with the zincate suggests the need for a solid phase to facilitate precipitation of the zinc sulfide.)

At 40 C, the rate of sulfide removal was extremely slow. At a ZnO/S ratio of 3, 60 minutes was required to remove 98 percent of the sulfur, while at a ratio of 1, only 38 percent was removed in 60 minutes.

These results strongly suggest that the reaction is limited by surface area and diffusion. A surprising result was the slow homogeneous reaction with sodium zincate. It may be that the $Zn(OH)_4^=$ ion present in the zincate solution reacted with some of the dissolved organic material (coal) and was not immediately available for reaction. The dried residue from the reaction was black. The zinc sulfide-zinc oxide recovered from the reactions involving ZnO powder ranged in color from brown (1:1 ratio) to light tan (3:1 ratio). Normally, both ZnS and ZnO are white.

The effect of surface area was demonstrated when a commercial grade (American process) zinc oxide was used instead of the reagent grade zinc oxide (4.0 m^2/g versus 7.0 m^2/g). Both reactions were run at 80 C and with a Zn/S ratio of 3. As shown in Table 17, the rate of sulfide removal for the commercial grade material was significantly

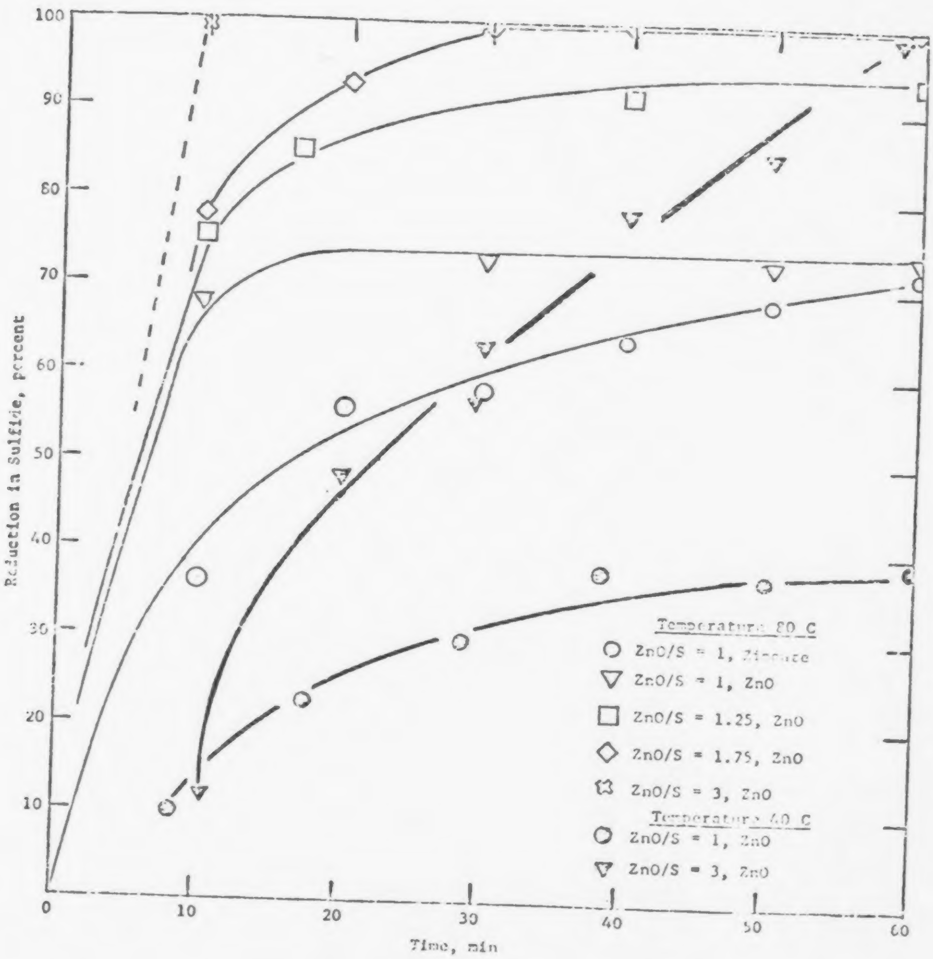

FIGURE 20. LEACHANT REGENERATION WITH ZnO (BATCH REACTION)

lower but sulfide removal was equally effective in 30 minutes.

Reaction of ZnO with the sulfide sulfur appeared to occur in two stages and was more pronounced with Na_2ZnO_2 than with ZnO. The first stage was rapid, occurring in a matter of a few minutes. The second stage was much slower, requiring possibly several hours at ambient temperature. This suggests a slow reaction mechanism or a competing reaction for the zinc. It may be possible to overcome this problem by conducting the desulfurization at higher temperatures.

Filtration of the final solution from the sodium zincate treatment was extremely slow, even with the precautions taken to limit solids in suspension by decantation. When ZnO powder was used, filtration was much less of a problem. The same behavior existed in the filtration of the reslurried ZnS during washing of both types of solids.

As indicated, problems associated with the use of sodium zincate were (1) low reaction rate for sulfide removal and (2) separation of zinc sulfide from the regenerated leachant. An attempt was made to overcome these problems by introducing zinc sulfide nuclei into the spent leachant before the addition of the zincate. Although the filtration problem was not eliminated entirely, sulfide removal was greatly improved at a Zn/S ratio of 1.25 as shown in Table 18. Complete sulfide removal was achieved at 80 C in less than 20 minutes. Under similar conditions, ZnO powder removed about 85 percent of the sulfur in 20 minutes.

Flow (Fixed-Bed) System. In the continuous regeneration system, where the spent leachant was passed through a bed of zinc oxide, removal of sulfide sulfur was essentially complete until the zinc oxide became coated with zinc sulfide, as noted in Table 19, at a Zn/S ratio of 3. Since the contact time in these experiments was about 3 minutes, the reaction of ZnO with Na_2S must be rapid. The use of pelletized zinc oxide* at Zn/S ratio of 3 and zinc oxide powder* at a Zn/S ratio of 1 was not as effective in removing the sulfide sulfur from the spent leachant.

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* Zinc oxide pellets are those produced by the American process (surface area of 4 m^2/g); zinc oxide powder is that produced by the French process (surface area of 7 m^2/g).

TABLE 17. COMPARISON OF THE RATE OF SULFIDE REMOVAL WITH ZINC OXIDE OF DIFFERENT SURFACE AREAS IN BATCH REACTOR (Zn TO S RATIO = 3; REACTION TEMPERATURE - 80 C)

Surface Area m^2/g	Percent Sulfide Removed for Various Times, Minutes					
	10	20	30	40	50	60
7	100	100	100	100	100	100
4	84.6	98.7	100	100	100	100

TABLE 18. EXTENT OF SULFIDE REMOVAL WITH SODIUM ZINCATE IN THE PRESENCE OF ZINC SULFIDE (Zn TO S RATIO= 1.25; REACTION TEMPERATURE = 80 C)

Experiment	Percent Sulfide Removed for Various Times, Minutes					
	0	10	20	30	40	50
33057-56	11.25	62.5	100	98.75	100	97.5

TABLE 19. REGENERATION EXPERIMENTS USING ZINC OXIDE IN A FIXED-BED REACTOR (REACTION TEMEPRATURE = 80 C; SOLUTION FLOW RATE - 5 ml/min)

Experiment	Zn to S Ratio(a)	Sulfide Ion Concentration for Increment(b), g/ℓ						
		0	1	2	3	4	5	6
33057-34	3	1.75	0	0	0	0	00.784	0.832
33057-40	1	1.75	1.216	1.040	0.928	0.848	0.944	0.816
33057-54	3(c)	1.25	0	0.032	0.144	0.256	0.48	---

(a) Mole ratio of the zinc in zinc oxide bed to sulfide ion present in 500 ml of spent leachant.

(b) Increment is the first 15 ml taken every 100 ml passed through the bed.

(c) Pelletized ZnO (American Process).

Residual Zinc in Regenerated Leachant. Because of the potential for contamination of the coal by zinc upon recycle of the regenerated leachant, the residual zinc concentration in the regenerated leachant was followed closely. Data for both the flow (continuous) system and the batch experiments are shown in Tables 20 and 21. In the flow system (Table 20), high zinc levels were associated with high sulfur removals as noted in Experiments 33057-34 and 33057-54. For example, 100 percent removal of the sulfide sulfur resulted in a zinc level in the leachant of 250 to 300 ppm. At lower degrees of sulfur removal, the zinc concentration in the spent leachant was significantly reduced.

The effect is not as pronounced in the batch-type experiments, as noted in Table 21. This may be due to coating of the zinc oxide particles with zinc sulfide as soon as they come in contact with the spent leachant. Therefore, the amount of zinc which dissolves appears to depend on the porosity of the zinc sulfide layer, on the zinc oxide, and on the Zn/S ratio.

Thus, these data suggest that a compromise must be made with respect to sulfur removal and zinc concentration in the regenerated leachant. Previous work on the Hydrothermal Coal Process has demonstrated that 100 percent removal of the sulfide sulfur is not necessary. Experimental results show that regenerated leachants containing about 0.13 percent sulfide sulfur can be recycled without any adverse effect on the degree of desulfurization.

Because of the cost of zinc oxide, recovery of the zinc values for recycle is essential. One potential approach is shown in Figure 21. Here, the zinc sulfide, after separation from the regenerated leachant, would be roasted at an elevated temperature of about 1900 F in an oxidizing atmosphere to convert the zinc sulfide to zinc oxide and sulfur dioxide according to the following reaction:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2.$$

The sulfur dioxide would be converted to sulfuric acid for marketing. The zinc oxide would be washed with water, to remove any zinc sulfate formed during the roasting operation, and recycled.

TABLE 20. ZINC CONCENTRATION AND SULFIDE REDUCTION IN REGENERATED LEACHANT (FLOW REACTOR, 5 ml/min, 80 C)

Experiment	Ratio ZnO/S	Sample Increment Interval											
		1(a)		2		3		4		5		6	
		Zn(b)	$S^{=}$(c)	Zn	$S^{=}$	Zn	$S^{=}$	Zn	$S^{=}$	Zn	$S^{=}$	Zn	$S^{=}$
33057-34	3(d)	N.D.(e)	100	305	100	275	100	315	100	8	55.2	6	52.5
33057-36	1(d)	10	75.3	6	---	5	---	---	63	---	10.4	N.D.	N.D.
33057-40	1(d)	N.D.	N.D.	30	84.9	10	65.4	7	60	6	42.3	N.D.	N.D.
33057-54	3(f)	240	100	83	97.4	4	88.5	3	79.5	3	61.5	N.D.	N.D.

(a) Average time interval between zero and 1 is 4 minutes and between 2-3, 3-4, 4-5, 25 minutes.

(b) mg/ℓ

(c) Reduction in sulfide, percent.

(d) ZnO powder (French grade, Baker).

(e) N.D. - not determined.

(f) ZnO powder/pellet (American grade, ASARCO).

TABLE 21. ZINC CONCENTRATION AND SULFIDE REDUCTION IN REGENERATED LEACHANT
(Batch Reactor)

		Sample Increment Interval											
	Ratio	1(a)		2		3		4		5		6	
Experiment	ZnO/S	Zn(b)	$S^=$(c)	Zn	$S^=$	Zn	$S^=$	Zn	$S^=$	Zn	$S^=$	Zn	$S^=$
Temperature 80 C													
33057-15	1.0(d)	16	65.9	22	51.6	18	98.6	22	53.1	24	54.4	25	72.8
33057-18	1.0(e)	50	58.8	63	71.5	46	74.4	85	81.3	84	71.5	24	72.9
33057-27	1.25(e)	5	71.1	5	82.3	ND(f)	100	5	100	ND	100	5	90.2
33057-50	1.75(e)	4	75.7	64	98.7	85	100	99	100	113	100	125	100
33057-46	3.0(e)	113	100	189	100	216	100	240	100	240	100	250	100
33057-56	1.25(d)	18	62.5	17	100	21	98.8	25	100	35	97.5	54	100
33057-52	3.0(g)	2	84.6	6	98.7	27	100	56	100	89	100	111	100
Temperature 40 C													
33057-42	1.0(e)	7	9.9	6	22.9	1	31.3	1	37.2	10	30.1	5	39.5
33057-44	3.0(e)	9	12.2	8	51.8	4	57.0	3	78.2	11	70.3	104	100

(a) Average time interval 10 minutes.

(b) Zinc concentration in mg/ℓ.

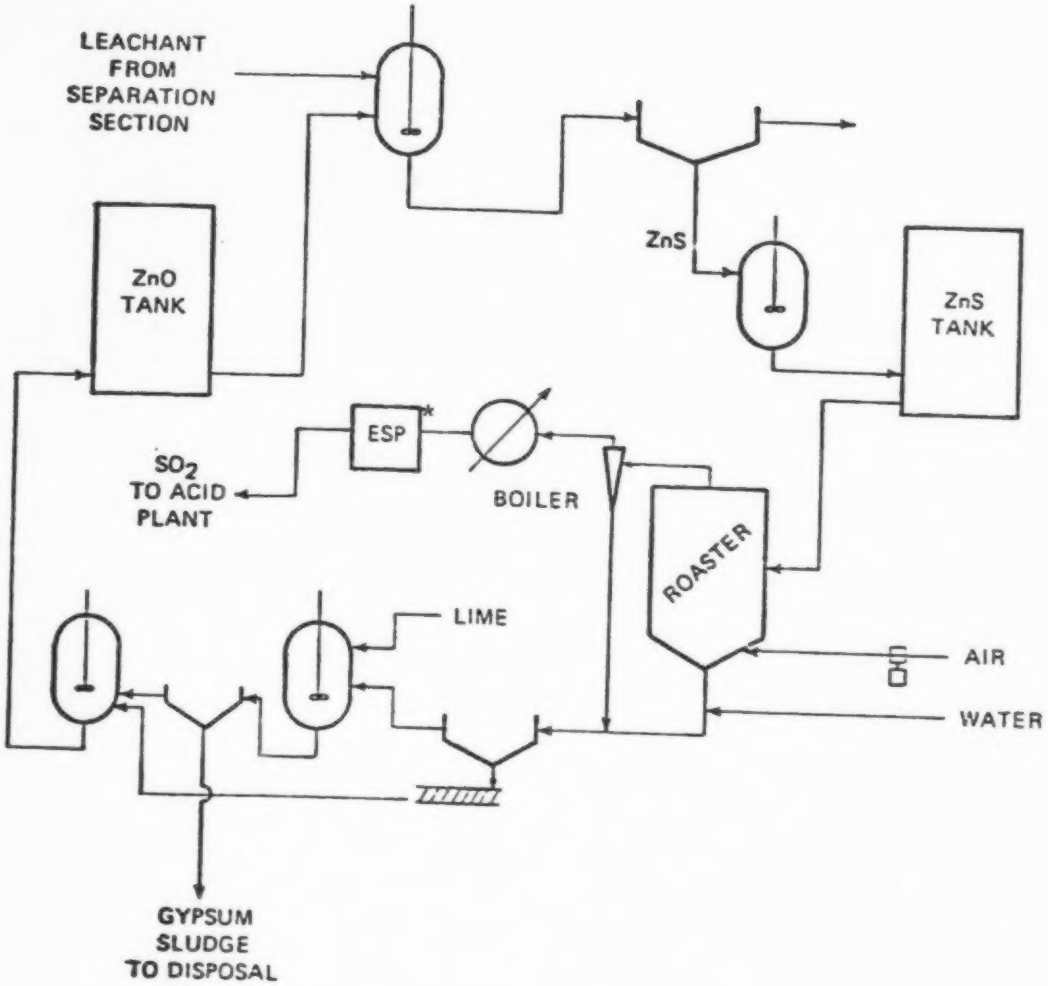
(c) Reduction in sulfide, percent.

(d) Sodium zincate in Experiment 15; zinc sulfide in sodium zincate in Experiment 56.

(e) AnO powder (French grade, Baker).

(f) ND - not determined.

(g) ZnO pelletized (American grade, ASARCO).


LEACHANT FROM SEPARATION SECTION
ZnO TANK
ZnS
ZnS TANK
ESP*
SO_2 TO ACID PLANT
BOILER
ROASTER
LIME
AIR
WATER
GYPSUM SLUDGE TO DISPOSAL

* Electrostatic Precipitator

FIGURE 21. POTENTIAL ZnO REGENERATION SECTION

Constituents carried down with the zinc sulfide that precipitated from the spent leachant along with foreign elements carried down with the precipitate, could be important considerations in selecting the method for regeneration of the zinc oxide. Therefore, several zinc sulfide precipitates were analyzed.

Analysis of Zinc Sulfide By-Products. The solid zinc sulfide by-products recovered from selected reactions in which either sodium zincate or zinc oxide were used as reagents to remove sulfide sulfur from the spent leachant were analyzed for sulfur, zinc, carbon, and sodium. Results are shown in Table 22. The solids recovered from the zincate regeneration reactions (Experiments 15 and 21) contained nearly stoichiometric amounts of sulfur and zinc (i.e., atomic ratio - 1.0). However, instead of being a white solid as zinc sulfide is known to be, the material was black. This probably resulted from organic material contained in or coprecipitated with the zinc sulfide. A C/Zn ratio greater than unity suggests that this may have been the case. In fact, since the reaction to remove sulfide sulfur from solution with sodium zincate was slower than that observed when solid zinc oxide was used, it is believed an organic complex of zinc may have formed first.

When solid zinc oxide was used as the reagent, the sulfur to zinc ratios of the products were lower, suggesting lower efficiency of zinc utilization. This was expected because the reaction probably was limited to the surface of the zinc oxide particle. For those reactions in which the ZnO/S ratio was 1.75 to 3.0, the S/Zn ratios of the ZnS products were correspondingly lower than for those reactions in which the ZnO/S ratio was 1.0, yet approached theoretical values of 0.33 and 0.57 for the 3 and 1.75 times stoichiometric cases (see Experiments 33057-46, -50, and -53-3, Table 22). The amount of carbon in the sulfide-oxide mixtures recovered from the reactions when zinc oxide was used suggest there was much less reaction with the organic portion of the spent leachant than when a zincate solution was used.

Sodium is retained by the solid but there does not appear to be a fixed pattern. Variability in the solids washing techniques probably accounts for the scatter in values. It would appear that good washing techniques and a coarse zinc oxide can keep the Na/Zn ratio

TABLE 22. ANALYSIS OF 'ZnS' PRECIPITATE FORMED DURING REGENERATION (Temp. 80 C; Batch System)

Experiment	ZnO/S Ratio	ZnO Source	Atomic Ratio S/Zn	Atomic Ratio Na/Zn	Atomic Ratio C/Zn
33057-15	1.0	Zincate	0.85	0.11	1.18
-19	1.0	French	0.70	0.03	0.16
-21	1.0	Zincate	0.97	0.17	1.45
-28	1.0	French	0.85	0.07	0.19
-46	3.0	French	0.28	0.17	0.05
-50	1.75	French	0.53	0.20	0.45
-53-3	3.0	American	0.29	0.02	0.29

around 0.02. When sodium zincate was used as a reagent, higher levels of sodium remained with the solid even when special attention was given to the washing procedure.

The solids recovered from the regeneration reactions with zinc oxide and sodium zincate were washed with water to remove residual regenerated leachant. As shown in Table 23, the washwater contained significant amounts of alkali and dissolved zinc.

Analysis of Regenerated Leachants. One criteria for defining the quality of the leachant regenerated by zinc oxide is the measure of the change that might occur in the distribution of the sulfur in the regenerated leachant. This evaluation is necessary because part of the sulfide sulfur might become oxidized to an oxysulfur anion during the regeneration reaction and give the impression that sulfide sulfur had been removed. Therefore, the difference in the amount of total sulfur and the amount of sulfide sulfur in the regenerated leachant should be close to the values observed in the feed spent leachant. (This difference provides a measure of the amount of sulfur in solution present

TABLE 23. ZINC AND ALKALI CONCENTRATIONS IN WASHWATER RECOVERED FROM SINGLE ZINC SULFIDE WASHING(a)

Experiment	Reactant	Alkali (NaOH) Concentration, g/1(a)	Zinc Concentration, mg/1(a
33057-7	Na_2ZnO_2	1.1	5
-18	ZnO	2.1	4
-21	Na_2ZnO_2	6.8	11
-24	ZnO (pelletized)	1.2	4
-27	ZnO	2.7	5
-34	ZnO	2.5	15
-36	ZnO	ND(b)	5
-42	ZnO	1.2	ND
-44	ZnO	2.4	ND
-46	ZnO	1.6	ND
-50	ZnO	1.5	ND
-52	ZnO (pelletized)	1.2	ND
-56	Na_2ZnO_2ZnS	3.3	ND

(a) All values for 150 ml of washwater diluted to 250 ml.

(b) ND - Not determined.

as oxysulfur anions.) The results of the analysis of regenerated solutions shown in Table 24 suggest that little, if any, oxidation of the sulfide ion occurs during regeneration with zinc oxide and that the sulfide sulfur is being removed during regeneration as zinc sulfide.

TABLE 24. QUALITY OF REGENERATED LEACHANT: COMPARISON OF DIFFERENCES IN TOTAL (S_T) AND SULFIDE (S_S) SULFUR IN ORIGINAL SPENT LEACHANT AND REGENERATED LEACHANTS: ZINC OXIDE SYSTEM

Experiment	Spent Leachant, g/ℓ			Regenerated Leachant, g/ℓ		
	$[S_T]$	$[S_S]$	Difference	$[S_T]$	$[S_S]$	Difference
33057-42	1.67	1.41 (1.25)(a)	0.26 (0.42)(b)	1.01	0.82	0.19
33057-44	1.67	1.41 (1.25)	0.26 (0.42)	0.38	0.0	0.38
33057-46	1.67	1.41 (1.25)	0.26 (0.42)	0.38	0.0	0.38
33057-50	1.39	1.25 (1.04)	0.14 (0.35)	0.31	0.0	0.31
33057-52	1.39	1.25 (1.04)	0.14 (0.35)	0.34	0.0	0.34

(a) Value for sulfide concentrations on samples where delay in analysis occurred.

(b) Differences using values in (a).

Leachant Regeneration with Iron Compounds

Prior work at Battelle had shown that ferrous compounds, such as $FeSO_3$, $Fe(OH)_2$, $FeSO_4$, removed sulfide sulfur from spent leachants with varying degrees of success. $FeSO_4$ was very effective, however, the spent leachant was contaminated with sodium sulfate. $FeSO_3$ removed about 50 percent of the sulfide sulfur, but the regenerated leachant was contaminated with sodium sulfite. $Fe(OH)_2$ was less effective, but the regenerated leachant was not contaminated with oxidized sulfur compounds.

Emphasis in this research was to be on the use of ferrous or ferric hydroxides, hydrated oxides, or a mixture of ferric and ferrous compounds and nonhydrated oxides. Other iron compounds were to be considered if the hydrated oxides systems were not effective. Activated elemental iron also was to be given consideration, if necessary.

Initial screening experiments with the iron compounds were conducted with a synthetic spent leachant containing 30 g/ℓ of NaOH and 2.63 g/ℓ of sulfide sulfur and with spent coal leachant as noted. The use of a synthetic leachant allowed visual observations to be made that were not possible when real spent leachant solutions were used.

The equipment and procedures described for zinc compounds were employed. Briefly, the iron compounds were added batchwise to 150-ml charges of synthetic or real spent leachant solutions. All experiments were conducted under a nitrogen atmosphere to prevent oxidation of the sulfide sulfur. The iron compounds usually were added to the solutions at 1 to 3 times stoichiometry, as determined by the amount of sulfide sulfur present. Samples of the solution were removed at the beginning, middle, and end of the 60-minute experiments, were centrifuged to remove solids, and then were analyzed for sulfide and total sulfur. (See Appendix 3-D.)

Iron Oxides. Results of the screening experiments with various iron oxides are shown in Table 25. A commercially available hydrated iron oxide [FeO(OH)] pigment with a goethite structure removed only 13 percent of the sulfide from the solution at 80 and 40 C at an FeO(OH)/S ratio of 3. The increase in total sulfur in the regenerated leachant from the amount present in the spent leachant may have been due to sulfate present in the pigment.

TABLE 25. IRON SYSTEM SCREENING EXPERIMENTS ON LEACHANT REGENERATION

				Feed					Regenerated Leachant		
Experiment	Fe-System	Stoichiometry, (Fe-X)/S Mole Ratio	Type[(a)]	S_T* g/ℓ	S_S** g/ℓ	NaOH g/ℓ	Temp., C	Time, min	S_T* g/ℓ	S_S g/ℓ	Percent Sulfide Reduction
33057-60	Pigment FeO(OH)	3, FeO(OH)/S	SL	3.13	2.88	60	80	8		2.5	13
								30		2.5	13
								60	3.56	2.5	13
33057-63	Pigment FeO(OH)	3, FeO(OH)/S	SL	3.13	2.88	60	40	8		2.49	13
								30		2.44	15
								60	3.56[(b)]	2.46	14
33057-65	Fresh $Fe(OH)_3$	3, $Fe(OH)_3/S$	SyL	2.78	2.63	30	23	8		1.02	61
								30		0.46	84
								60	ND	0.28	90
33057-70	Fresh $Fe(OH)_3$	3, $Fe(OH)_3/S$	SyL	2.78	2.63	30	80	8		1.21	54
								30		1.59	40
								60	1.77	1.68	36
33057-73	Fresh $Fe(OH)_3$	3, $Fe(OH)_3/S$	Syl	2.78	2.63	30	0	8		1.15	56
								30		1.12	(57)
								60	0.48	0.19	93
33057-78	Fresh $Fe(OH)_2$	3, $Fe(OH)_2/S$	Syl	2.78	2.63	30	29	8		1.34	49
								30		0.70	73
								60	0.83	0.54	79
33057-80	Regenerated $Fe(OH)_3$[(c)]	3, $Fe(OH)_x/S$	SyL	2.78	2.63	30	29	8		2.08	21
								30		1.92	27
								60	ND	1.69	36
33057-82	Fresh $Fe(OH)_2$	3, $Fe(OH)_2/S$	SyL	2.78	2.63	30	0	8		1.2	54
								30		1.07	59
								60	ND	0.96	64
33057-85	Fe_2O_3	1, Fe_2O_3/S	SyL	2.78	2.63	30	29	8	ND	2.4	9
		3, Fe_2O_3/S	SyL	2.78	2.63	30	29	8	2.81	1.2	56
33057-87	Fe	3, Fe/S	SyL	3.13	2.49	60	29	8	ND	2.49	0
33057-86	Fresh $Fe(OH)_2$	3, $Fe(OH)_2/S$	SL	3.13	2.49	60	29	8		1.54	42
								30		0.77	71
								60	1.39	0.51	81

(a) SL, Spent Leachant from coal desulfurization; SyL, Synthetic Leachant made from NaOH and $Na_2S \cdot 9H_2O$

(b) Value based on S_T of regenerated leach from 33057-60.

(c) Regenerated by treatment of solids recovered from Experiment 33057-73.

* S_T = total sulfur concentration; S_s = sulfide sulfur concentration.

Freshly prepared ferric hydroxide was more effective than FeO(OH). Approximately 90 percent of the sulfide sulfur was removed from a synthetic leachant at 0 and 23 C. This material was not effective at 80 C as is shown in Figure 22. This behavior suggested that reversal of the sulfide removal reaction might be possible at slightly elevated temperatures. This reversal was seen to offer a potential method of regenerating ferric hydroxide from the precipitated iron sulfide. For these experiments, the extent of side reactions in which the sulfide sulfur was converted to an oxidized sulfur species appeared to be low, as can be seen by comparing $(S_T\text{-}S_S)^*$ for feed solution with $[S_T\text{-}S_S]$ for regenerated leachant.

Assuming ferric hydroxide reacts with Na_2S in the spent leachant according to the following reaction:

$$2Fe(OH)_3 + 3Na_2S \xrightarrow{H_2O} Fe_2S_3 + 6NaOH \ ,$$

results indicate a reversal which would regenerate the iron hydroxide by the following reaction:

$$Fe_2S_3 + 6H_2O \xrightarrow{100\ C} 3H_2S\uparrow + 2Fe(OH)_3\downarrow \ .$$

If this were the case, the H_2S could be converted to elemental sulfur by the Claus process and the $Fe(OH)_3$ could be recycled. Thus, several experiments were run to check on this recycle scheme.

As shown in Figure 23, 36 percent of the sulfide sulfur was removed from a synthetic spent leachant by a regenerated iron sulfide product from Experiment 33057-73. In this case, the iron sulfide product was regenerated by heating it in the presence of water and CO_2 at 100 C. Carbon dioxide was used in an effort to increase the degree of conversion of the iron sulfide product to ferric hydroxide. Hydrogen sulfide was one of the reaction products and the amount released was measured. Composition of the regenerated iron compound was not determined.

Freshly prepared ferrous hydroxide $[Fe(OH)_2]$ appears to be less effective than freshly prepared ferric hydroxide for removal of sulfide

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* S_T = total sulfur concentration; S_S = sulfide sulfur concentration.

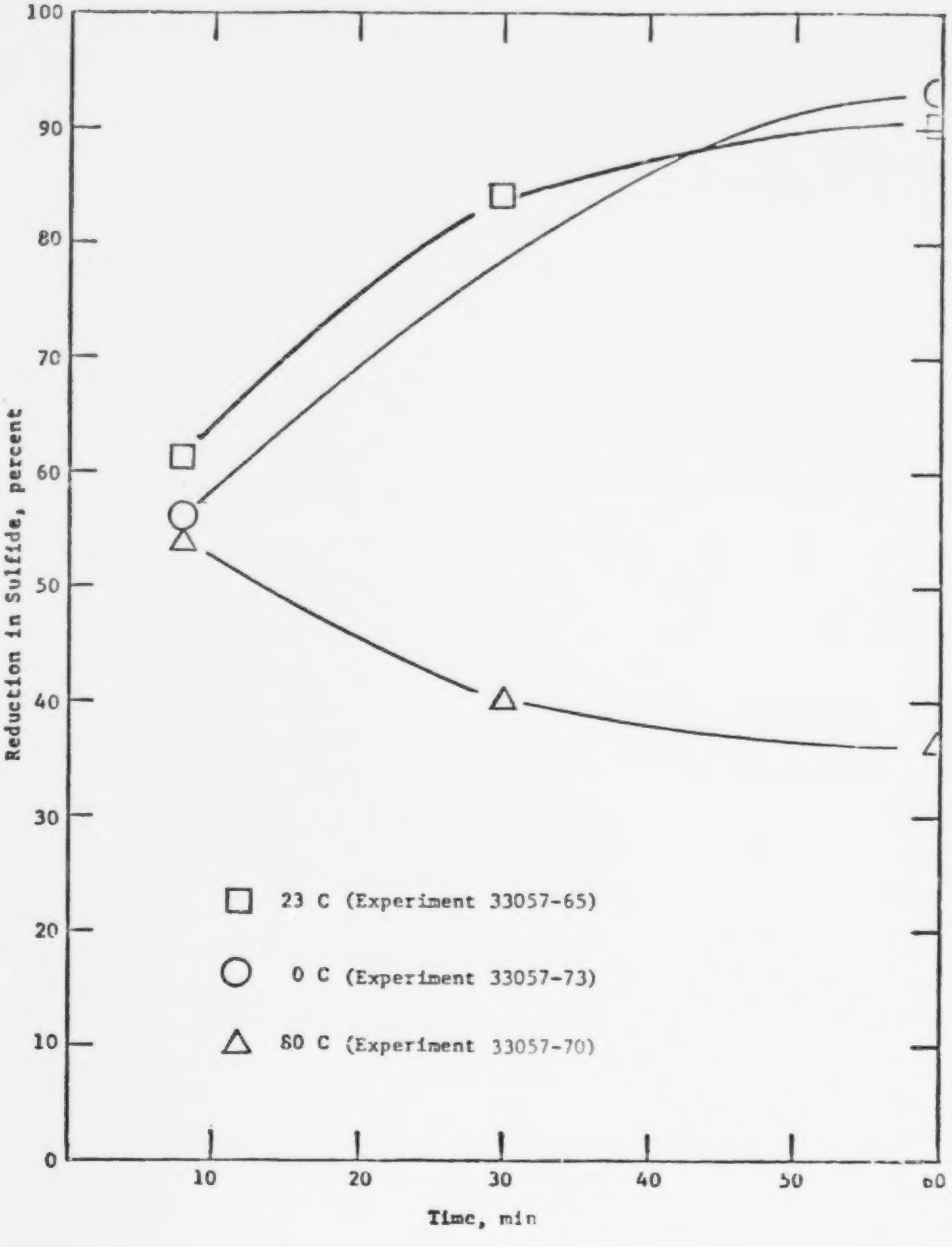

FIGURE 22. THE EFFECT OF TEMPERATURE ON SYNTHETIC LEACHANT REGENERATION WITH $Fe(OH)_3$

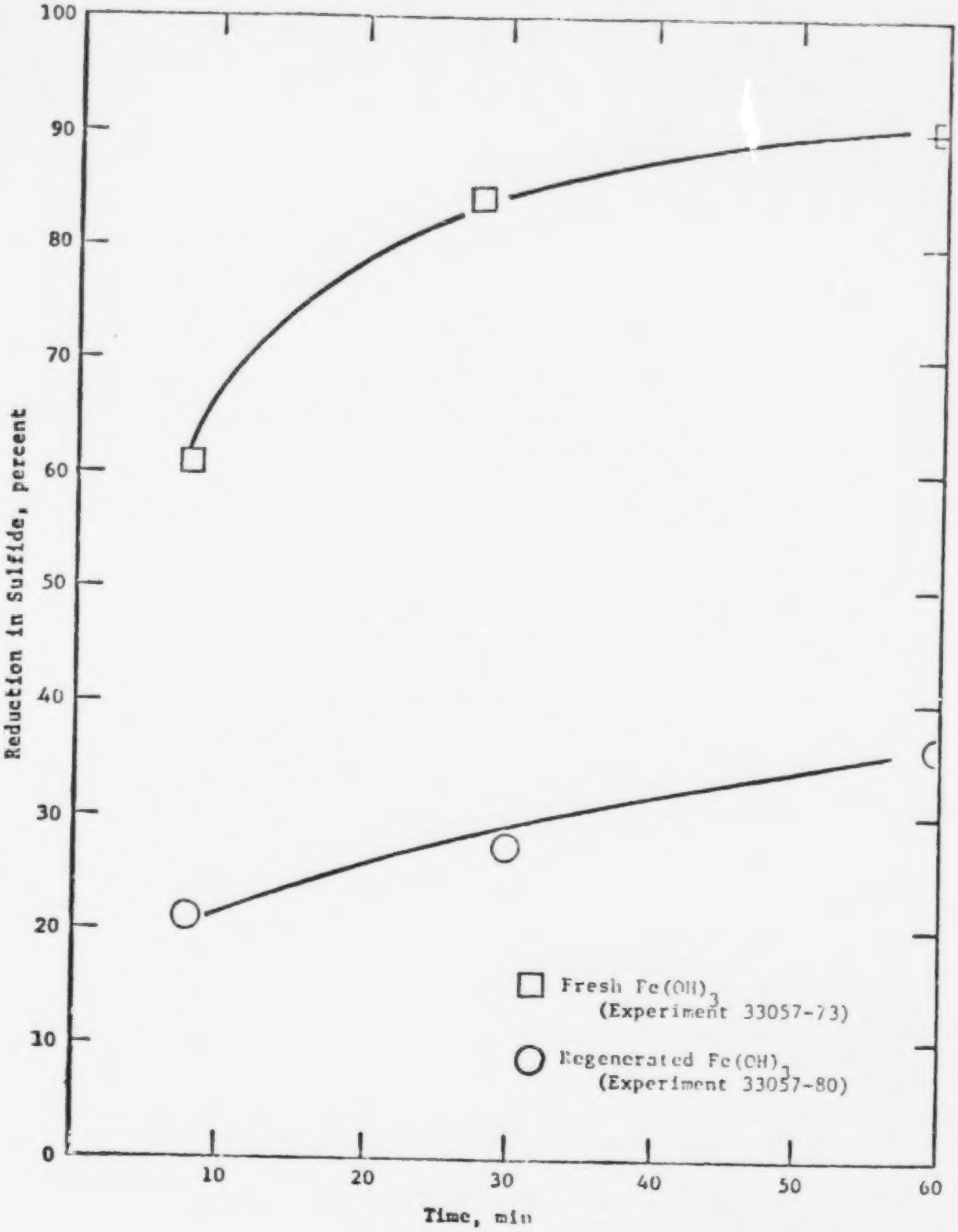

FIGURE 23. COMPARISON OF SULFIDE REMOVAL FROM SYNTHETIC LEACHANT WITH FRESH AND REGENERATED $FE(OH)_3$

from a synthetic spent leachant, as noted in Table 25. For example, ferrous hydroxide removed 79 percent of the sulfide sulfur at 23 C and 64 percent at 0 C in 60 minutes, whereas ferric hydroxide removed about 90 percent of the sulfide sulfur at 23 and 0 C in the same period of time. However, ferrous hydroxide appears to be equally as effective on synthetic and real spent leachants (Experiments 33057-78 and -86).

Reagent grade ferric oxide (Fe_2O_3) was not effective in precipitating sulfide sulfur from a synthetic spent leachant, as shown in Experiment 33057-85, at Fe_2O_3/S ratios of 1 and 3 in 8 minutes. The 56 percent reduction of sulfide sulfur at a ratio of 3 appeared to result from oxidation of the sulfide ion rather than the precipitation of an iron sulfide.

Elemental iron powder did not appear to remove sulfide when used as-received (Experiment 33057-86). The surface may have been coated with an unreactive iron oxide.

Iron Hydroxides. The results of the remaining screening experiments in which ferric hydroxide was used are given in Table 26. Fresh unheated ferric hydroxide, ferric hydroxide that had been heated, and a regenerated ferric hydroxide were evaluated. Reactions were run at 0, 24, and 27 C with real and synthetic leachant solutions. The criterion used to evaluate the performance of ferric hydroxide was the reduction of both the sulfide ion concentration $[S^=]$ and the total sulfur concentration $[S_T]$, simultaneously. Potentially, the ferric ion can oxidize the sulfide ion to an oxysulfur anion during the regeneration reaction rather than remove it as an iron xulfide. Hence, this oxidation reaction had to be minimized.

The data in Table 26 indicate that the freshly prepared hydroxide was as effective for desulfurization of real spent leachant as the synthetic spent leachant. In Experiments 33057-92 and 33179-23, 90 and 98 percent, respectively, of the sulfide was removed at room temperature in one hour. When the reaction temperature was reduced to 0 C, less consistent behavior was observed. In Experiment 33057-94, 51 percent of the sulfide was removed, while in Experiment 33179-22, 79 per-

TABLE 26. FERRIC HYDROXIDE SCREENING EXPERIMENTS ON SPENT LEACHANT REGENERATION

		Stoichiometry	Leachant Characteristics						Regenerated Leachant		
Experiment	Fe-System	Mole Ratio $Fe(OH)_3/S$	Type[a]	g/ℓ	g/ℓ	g/ℓ	Temp. C	Time, min	$S_T^=$ g/ℓ	$S_S^=$ g/ℓ	Percent Sulfide Reduction[b]
33057-92	Fresh $Fe(OH)_3$	3	SL	3.13	2.56	60	27	8		1.09	58
								30		0.38	85
								60	1.11	0.26	90
33057-94	Fresh $Fe(OH)_3$	3	SL	3.13	2.56	60	0	8		2.09	18
								30		1.41	45
								60	1.43	1.26	51
33057-96	Fresh $Fe(OH)_3$	3	SyL	2.78	2.63	60	27	8		1.09	59
							0	13		0.93	65
							0	43		0.86	67
							0	73	ND	0.32	88
33067-98	Fresh $Fe(OH)_3$[c]	3	SyL	2.78	2.63	60	27	8		1.86	29
								30		1.73	34
								60	ND	1.57	40
33179-5	Fresh $Fe(OH)_3$[c]	3	SyL	2.78	2.63	60	27	8		2.30	12
								30		2.05	22
								60	1.76	1.70	36
								(24 hr)[d]		1.50	43
33179-7	Regenerated, $Fe(OH)_3$ from 33179-5	3	SyL	2.78	2.63	60	27	8		2.56	0
								30		2.54	1.7
								60	2.78	2.40	7.3
33179-9	Fresh $Fe(OH)_3$[c]	3	SyL	2.78	2.63	60	27	8		2.21	16.0
								30		1.97	25.0
								60	1.67	1.38	47.5
33179-22	Fresh $Fe(OH)_3$	3	SL	2.18	1.78		0	8		0.61	65
								30		0.35	80
								60	0.76	0.38	79
33179-23	Fresh $Fe(OH)_3$	3	SL	2.18	1.78		24	8		0.58	68
								30		0.29	84
								60	0.62	0.03	98
33179-24	Fresh $Fe(OH)_3$	3	SyL	2.78	2.53		24	8		1.47	42
								30		1.31	48
								60	1.51	0.93	63

(a) SL, spent leachant from coal desulfurization; SyL, synthetic leachant made from NaOH and $Na_2S \cdot 9H_2O$.

(b) Uncorrected for any oxidized sulfur formed during the regeneration.

(c) $Fe(OH)_3$ boiled, ppt no longer gel-like.

(d) Apparent reduction in sulfide concentration due to removal of colloidal iron sulfide from suspension after 24 hours.

cent of the sulfide was removed. Apparently, the rate of reaction is lower at 0 C than at room temperature.

While the ferric hydroxide was heated to boiling during its preparation, the precipitate was no longer gel-like, but reverted to a hydrated ferric oxide material. This made filtration and subsequent use of the material easier. However, its reactivity with synthetic spent leachant decreased and the amount of sulfide removed was below 50 percent (see Experiments 33057-98, 33179-5, and -9). When the spent ferric hydroxide recovered from Experiment 33179-5 was regenerated by treating it in boiling water and CO_2, the regenerated oxide had essentially no reactivity with synthetic spent leach solution (see Experiment 33179-7).

The data from the screening experiments on ferrous and ferric hydroxide performance were used to calculate the extent that sulfide sulfur oxidation may have contributed to the apparent overall sulfur removal. Although the results of the calculations (see Table 27) indicate that some oxidation of the sulfide occurred during the regeneration, the data are inconclusive. Oxidation may have resulted from inadvertent exposure of the leachant to atmospheric oxygen, which might account for the wide variation in the degree of sulfide sulfur oxidation. On the other hand, oxidation may have resulted from reaction of the sulfide sulfur with the ferric or ferrous hydroxides. However, $Fe(OH)_2$ would not be expected to oxidize sulfide sulfur to the same or even greater degree than does $Fe(OH)_3$. Therefore, more work is required on this facet of the leachant regeneration before a definite conclusion can be drawn with respect to the extent sulfide sulfur may be oxidized by these compounds.

As mentioned previously, attempts at regenerating spent ferric hydroxide recovered from synthetic spent leachant experiments produced a less gel-like (more crystalline) material with greatly reduced activity. Results suggest that the material would degrade further with each regeneration cycle. Therefore, the possibility that this procedure would provide a reactive, recyclable source of hydrated iron oxide appeared slight.

The lack of a method for regeneration of an active reagent suggested that perhaps an open-ended process, in which the sulfide contain-

TABLE 27. SULFIDE OXIDATION AS PERCENT OF SULFUR REMOVAL

Experiment	Fe-System	Temp, C	S = Sulfide Removal S_S (Feed) - S_S (Prod) g/ℓ	S_{ox} - Oxidized Sulfur $(S_T-S_S)_{Prod}$ - (S_T-S_S) Feed g/ℓ	Percent S_{ox}/S
33057-73 (SyL)(a)	$Fe(OH)_3$	0	2.44	(0.29 - 0.15)	5.7
33057-78 (SyL)	$Fe(OH)_2$	29	2.09	(0.29 - 0.15)	6.7
33057-86 (SL)	$Fe(OH)_2$	29	1.98	(0.88 - 0.64)	12.1
33057192 (SL)	$Fe(OH)_3$	27	2.30	(0.85 - 0.57)	12.2
33057-94 (SL)	$Fe(OH)_3$	0	1.30	(0.17 - 0.57)	See (b)
33179-22 (SL)	$Fe(OH)_3$	0	1.40	(0.38 - 0.4)	1.4
33179-23 (SL)	$Fe(OH)_3$	24	1.75	(0.59 - 0.4)	11.0
33179-24 (SyL)	$Fe(OH)_3$	24	1.60	(0.58 - 0.25)	14.4

(a) SyL, synthetic spent leachant; SL, spent leachant.

(b) Values for S_{ox} were negative.

ing iron hydroxide would be discarded, should be considered. This would require that less expensive sources of iron, including compounds and various forms of elemental iron, be screened.

Materials Containing Iron. The experiments in which materials containing iron were screened for their ability to remove sulfide ion from synthetic spent leachant were conducted in capped, 15-ml centrifuge tubes. Fixed amounts of synthetic spent leachant solution were added to the nitrogen-purged tubes containing the material being evaluated. The capped tubes were shaken for periods up to 60 minutes at 25 to 27 C. The tubes were centrifuged and the supernatant solution was analyzed for residual sulfide ion concentration.

The results of experiments with synthetic spent leachant which were used to screen rapidly iron-containing materials as an alternative to the use of ferric hydroxide in the open ended process are given in Table 28. In Experiments 33170-1, -3, -5, and -7, an attempt was made to improve on the activity of Fe_2O_3 by exposing the oxide to various combinations of air, water, nitrogen, and hydrogen at 440 C. (Activity here was measured only by a reduction in sulfide concentration and not a reduction in total sulfur concentration.) No significant improvement over the untreated oxide was observed. Hematite ore (Experiment 33170-8) performed about the same way as Fe_2O_3 powder. Fly ash exhibited some removal activity and may have some potential as a disposal reagent if sodium hydroxide does not attack it. Since the removal levels were modest, further work on the concept was delayed. Coal ground to -50 mesh exhibited some sulfide removal capability; however, it is suspected that air occluded in the coal may have caused the apparent 33 percent reduction in sulfide ion concentration by forming oxysulfur anions. Zero valent iron in iron carbonyl did not remove sulfide ion. However, iron powder that had been pretreated with hydrogen at 400 C exhibited some activity and reduced the sulfide ion concentration 16 percent (see Experiment 33170-10).

The results of this preliminary screening experiment suggested that active forms of reduced iron might be worth further screening.

TABLE 30. ADDITIONAL ELEMENTAL IRON SCREENING EXPERIMENTS ON SPENT LEACHANT REGENERATION

Experiment	Fe-System Temperature of Reduction, C	Stoichiometry, Fe/S Mole Ratio	Feed						Regenerated Leachant		
			Type(a)	S_T g/ℓ	S_S^- g/ℓ	NaOH g/ℓ	Temp. °C	Time, min	S_T g/ℓ	$S_S^=$ g/ℓ	Percent Sulfide Reduction
33179-36	Reduced Fe_2O_3, 460 C, H_2O flow 100 cc/min.	11.0	SL	2.18	1.78	25	80	8		1.50	16
								30		1.47	17
								60	ND	1.06	41
33179-37	Regenerated Spent Iron Oxide H_2 flow 100 cc/min.	8.0	SL	2.18	1.78	25	80	8		1.60	10
								30		1.41	21
								60	ND	1.28	28
33179-38	Reduced Fe_2O_3, 460 C, H_2 flow 100 cc/min.	8.0	SL	2.18	1.78	25	80	8		1.50	16
								30		1.33	25
								60	ND	1.14	36
33179-39	Reduced Fe_2O_3, 460 C, H_2 flow 100 cc/min.	19.0	SL	2.47	2.07	25	80	8		1.70	18
								30		1.38	34
								60	ND	0.96	54
33179-40	Reduced Fe_2O_3, 400 C, H_2 flow 100 cc/min.	15.0	SL	2.47	2.07	25	80	8		1.87	10
								30		1.62	22
								60	ND	1.31	37
33179-41	Reduced Fe_2O_3, 400 C, H_2 flow 100 cc/min.	13.0	SL	2.47	2.07	25	80	8		1.98	4
								30		1.83	11
								60	ND	1.68	19
33179-46	Reduced Fe_2O_3, 400 C, H_2 flow 5 cc/min.	13.0	SL	2.47	2.07	25	80	8		1.87	10
								30		1.79	14
								60	ND	1.84	10
33179-47	Reduced Fe_2O_3, 400 C, H_2 flow 30 cc/min	17.0	SL	2.47	2.07	25	80	8		1.99	4
								30		2.06	0
								60	ND	2.05	0
33179-52	Commercial Fe_2O_3	17.0	SL	2.47	2.07	25	80	8		1.84	11
								30		1.79	13
								60	ND	1.66	20
33179-53	Reduced/Oxidized (<1 min.) Fe_2O_3, 400 C, H_2 flow 100 cc/min.	14	SL	2.47	2.07	25	80	8		1.81	13
								30		1.51	27
								60	ND	1.41	32

TABLE 30. (CONTINUED)

Experiment	Fe-System Temperature of Reduction, C	Stoichiometry, Fe/S Mole Ratio	Feed				Temp., C	Time, min.	Regenerated Leachant		
			Type[(a)]	S_T g/ℓ	$S_S^=$ g/ℓ	NaOH g/ℓ			S_T g/ℓ	$S_S^=$ g/ℓ	Percent Sulfide Reduction
33179-56	Reduced/Oxidized (5 min) Fe_2O_3, 400, H_2 flow 100 cc/min.	14	SL	2.47	2.07	25	80	10		1.02	50.7
								30		0.58	71.9
								70	0.89	0.38	81.5
33179-57	Reduced/Oxidized (5 min) Fe_2O_3, 460 C, H_2 flow 100 cc/min.	19	SL	2.47	2.07	25	80	12		1.92	7.2
								23		1.84	11.1
								60	0.76	0.224	89.2
								filtrate			(97.7)
33179-58	Reduced/Oxidized (15 min) Fe_2O_3, 400 C, H_2 flow 100 cc/min.	19	SL	2.47	2.07	25	80	12		1.44	30.4
								30		1.55	25.0
								62	ND	1.53	25.8
33179-59	Reduced/Oxidized (5 min) Fe_2O_3 , 400 C, H_2 flow 100 cc/min.	20	SL	2.47	2.07	25	80	9		1.7	17.9
								25		1.28	38.2
								54	ND	0.67	66.8
33179-60	Reduced/Oxidized (9 min.) Fe_2O_3, 400 C, H_2 flow 100 cc/min.	20	SL	2.47	2.07	25	80	14		2.00	3.4
								35		1.35	34.8
								62		1.06	48.5
								92	ND	0.89	57.2
33179-61	Reduced/Oxidized (1 min) Fe_2O_3, 400 C, H_2 flow 100 cc/min	20	SL	2.83	2.26	28	80	10		1.97	13.1
								30		1.6	29.3
								61		1.14	49.8
								90	ND	0.69	69.6
33179-62	Reduced/Oxidized (3 min) Fe_2O_3, 400 C, H_2 flow 100 cc/min	19	SL	2.83	2.26	28	80	8		1.44	36.4
								32		0.86	61.8
								61	0.91	0.34	85.2
33179-63	Reduced/Oxidized (3 min) Spent Fe_2O_3 from 33179-62 400 C, H_2 flow 100 cc/min	11	SL	2.83	2.26	28	80	9		1.36	39.8
								29	0.56		75.2
								60	ND	0.32	85.8
33179-64	Reduced/Oxidized (3 min) Spent Fe_2O_3 from 33179-63, 400 C, H_2 flow 100 cc/min	8	SL	2.83	2.26	28	80	8		1.41	37
								30		0.80	64
								60	ND	0.48	79
33179-65	Reduced/Oxidized (3 min) Fe_2O_3, 400 C, H_2 flow 100 cc/min	14	SL	2.83	2.26	28	100	8		1.88	16
								30		1.33	41
								60	ND	0.99	56
33179-66	Reduced/Oxidized (3 min) Fe_2O_3, 400 C, H_2 flow 100 cc/min	11	SL	2.83	2.26	28	80	8		1.90	16
								30		1.54	32
								60		1.06	53
								90	ND	0.67	70
33179-67	Fe_3O_4, from reduction of Fe_2O_3 400 C, H_2 + H_2O at 40 C	18	SL	2.83	2.26	28	80	8		2.02	11
								30		2.08	8
								60		2.05	9
								90	ND	1.86	18

(a) SyL, synthetic spent leachant; SL, spent leachant.

was exposed to the atmosphere for a specific time before introducing it into the spent leachant.

Analysis of these data suggests that partial oxidation of the reduced-iron oxide by exposure to the atmosphere is necessary to effect removal of the sulfide sulfur from the spent leachant. Maximum sulfide removal was about 54 percent in 60 minutes (Experiment 33179-39) at an Fe/S ratio of 19. This was achieved with the reduced-iron oxide that had not been exposed to the atmosphere. When the hydrogen flow rate, reduction temperature, and reduction time were varied, less sulfide sulfur was removed.

On the other hand, when reduced-iron oxide was exposed to the atmosphere prior to reacting it with the spent leachant, up to about 80 to 90 percent of the sulfide sulfur was removed in 60 minutes. (Experiments 33179-62 and 33179-57). Untreated iron oxide removed about 20 percent of the sulfide sulfur in 60 minutes (Experiment 33179-52).

The degree of oxidation as related to time of exposure of the reduced iron oxide to the atmosphere had a significant effect on the degree of sulfur removal, as shown in Experiments 33179-53 through -66. (In these experiments, reductions were carried out at 400 C using a hydrogen flow rate of 100 cc/min. The amount of surface area exposed was kept uniform in all but a few cases.) These data, and those shown in Figure 24 suggest that an exposure of the reduced oxide to air for 3 to 5 minutes yields a material with activity for removing sulfide ion from the solution. After mixing with the spent leachant for 60 minutes, the material removed between 82 and 89 percent of the sulfide (see Experiments 33179-56, -57, and -62). This reduction in the total sulfur also was achieved with only slight evidence for the oxidation of sulfide to a nonsulfide species (i.e., to an oxysulfur anion). Exposure of the reduced iron oxide for longer and shorter periods of time without stirring resulted in the removal of less sulfide sulfur (Experiments 33179-58, -60, and -61).

Normally, the reduced iron oxide, after cooling in a nitrogen atmosphere, was transferred to a quartz boat and allowed to react with the atmospheric oxygen, without stirring, for a specific time. However,

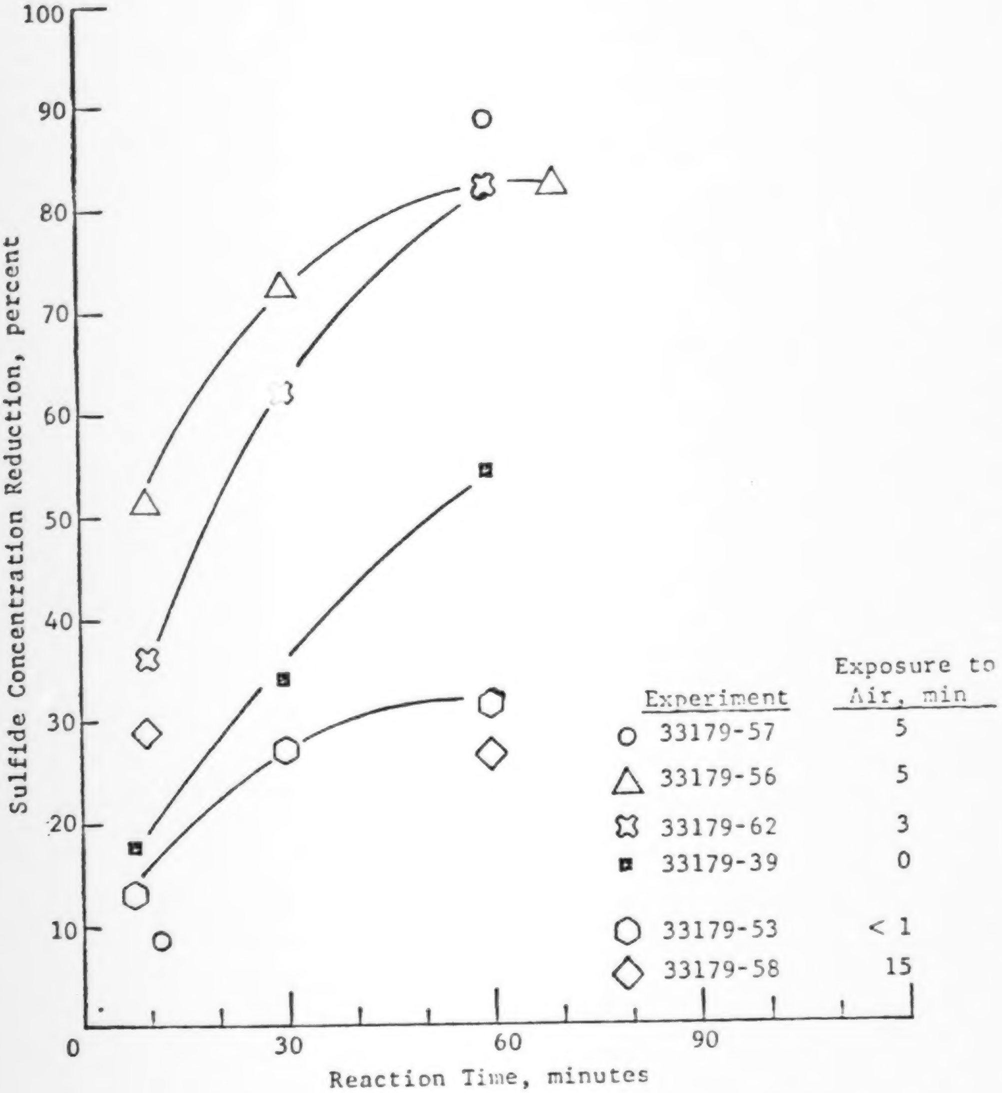

FIGURE 24. EFFECT OF THE PERIODS OF EXPOSURE TO AIR OF REDUCED IRON OXIDE ON REDUCTION IN SULFIDE CONCENTRATION

in Experiments 33179-59 and -66, the material, exposed for 5 and 3 minutes, respectively, was stirred during oxidation. This appeared to result in over-oxidation of the reduced iron oxide as deduced from the decrease in sulfide removal.

In an attempt to pinpoint the active species involved in sulfide removal (Experiment 33179-67), Fe_3O_4 prepared from Fe_2O_3 using hydrogen and water vapor (hydrogen passed through water at 40 C) was tried. The result (removal of 18 percent of the sulfide sulfur in 90 minutes) suggested that this species alone was not the active agent.

Preliminary results indicated that the spent reduced iron oxide could be regenerated for recycle. In Experiment 33179-63, the spent reduced iron oxide recovered from Experiment 33179-62 was treated in hydrogen and exposed to air again. This regenerated material proved to be equally as effective for sulfide removal as the original reduced/oxidized iron oxide. After 60 minutes, 85.8 percent of the sulfide was removed from a fresh batch of spent leachant. The material recovered the second time (from Experiment 33179-63) showed a slightly lower activity than the original material, after the reduction-air exposure treatment (i.e., 79 percent removal observed in Experiment 33179-64). The lower value of 79 percent may have been due to the decrease in the Fe/S ratio from 11 to 8. These results, summarized in Figure 25, suggest that regeneration of the reduced iron oxide is possible and that the performance of the regenerated material is comparable to the original material for at least two cycles.

The fate of the sulfur removed by the reduced oxide is not clearly understood. After reduction, there is evidence that it is retained by the spent iron oxide regenerant: no H_2S is evolved during the treatment with hydrogen. Further work to establish the sulfur balance is needed before details of this approach can be finalized.

Thus, the results of the experiments on the use of the iron system to regenerate the spent leachant were:

- Commercially available Fe_2O_3 provided a low level of sulfide removal capability (Experiment 33179-52 in Table 30).

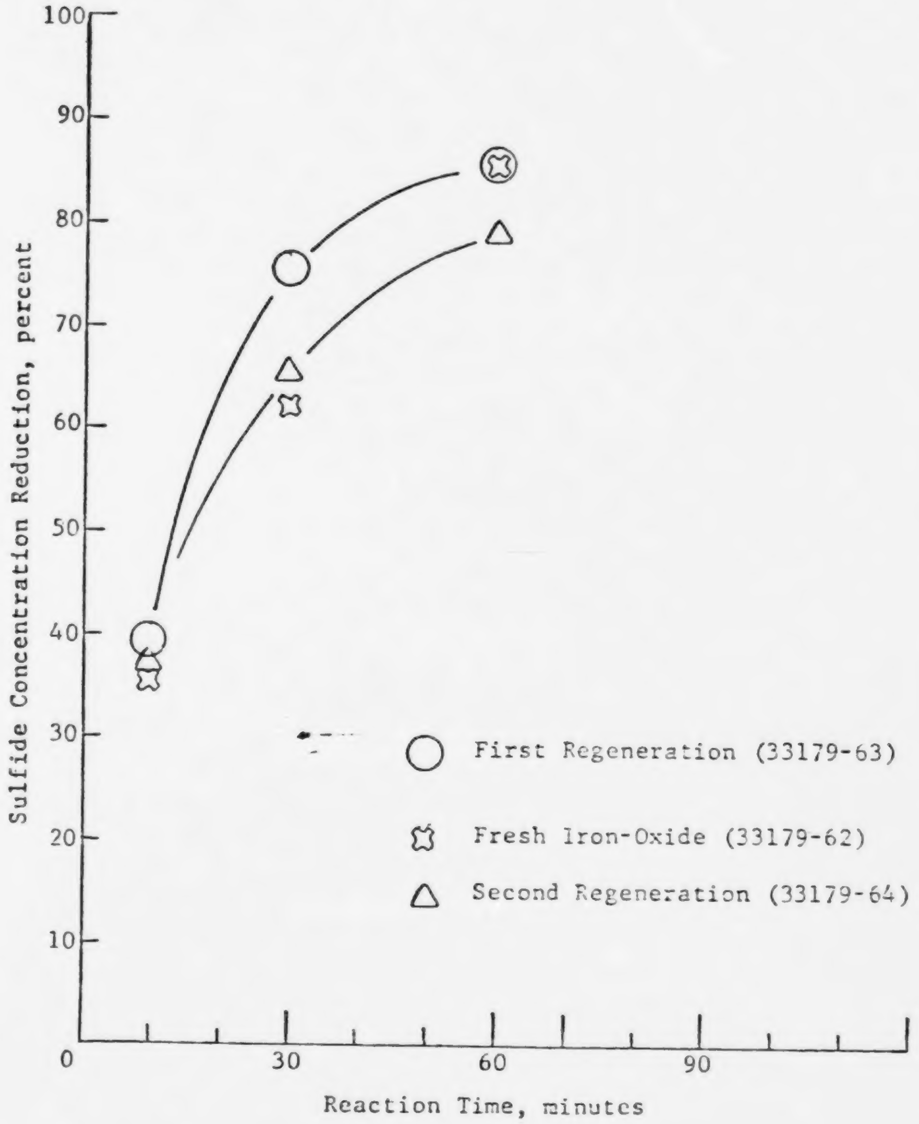

FIGURE 25. EFFECT OF REGENERATION OF SPENT IRON OXIDE

- When Fe_2O_3 was reduced under conditions known to form "FeO" (i.e., hydrogen reduction at 300 C), the observed product was not pyrophoric as expected and a low level of activity for sulfide removal was observed. There appeared to be an induction period of > 8 minutes before removal was observed (Experiment 33179-22, Table 26).
- When Fe_2O_3 was reduced under conditions known to produce Fe_3O_4, the product had a low activity for sulfur removal. The amount removed remained about the same for the first 50 minutes and then increased (Experiment 33179-67).
- When Fe_2O_3 was reduced under conditions known to yield elemental pyrophoric iron and the product was added directly to spent leachant without exposure to air, the material exhibited moderate activity for sulfide removal. The rate of removal appeared to be higher than rates for "FeO", Fe_3O_4, and Fe_2O_3 (see Figure 26).
- When the product from the reduction of Fe_2O_3 to pyrophoric iron was exposed to air for periods of 1 to 5 minutes, the material exhibited high levels of activity for sulfide removal. Exposures < 1 minute and 9 minutes or greater produced a material with activities between those of untreated iron oxide and the oxides of iron (see Figure 24).
- Earlier experiments using either $Fe(OH)_2$ or $Fe(OH)_3$ have demonstrated the high level of activity for sulfide removal of these oxides, e.g., 90 percent removal in 60 minutes (Experiment 33179-23, Table 26).

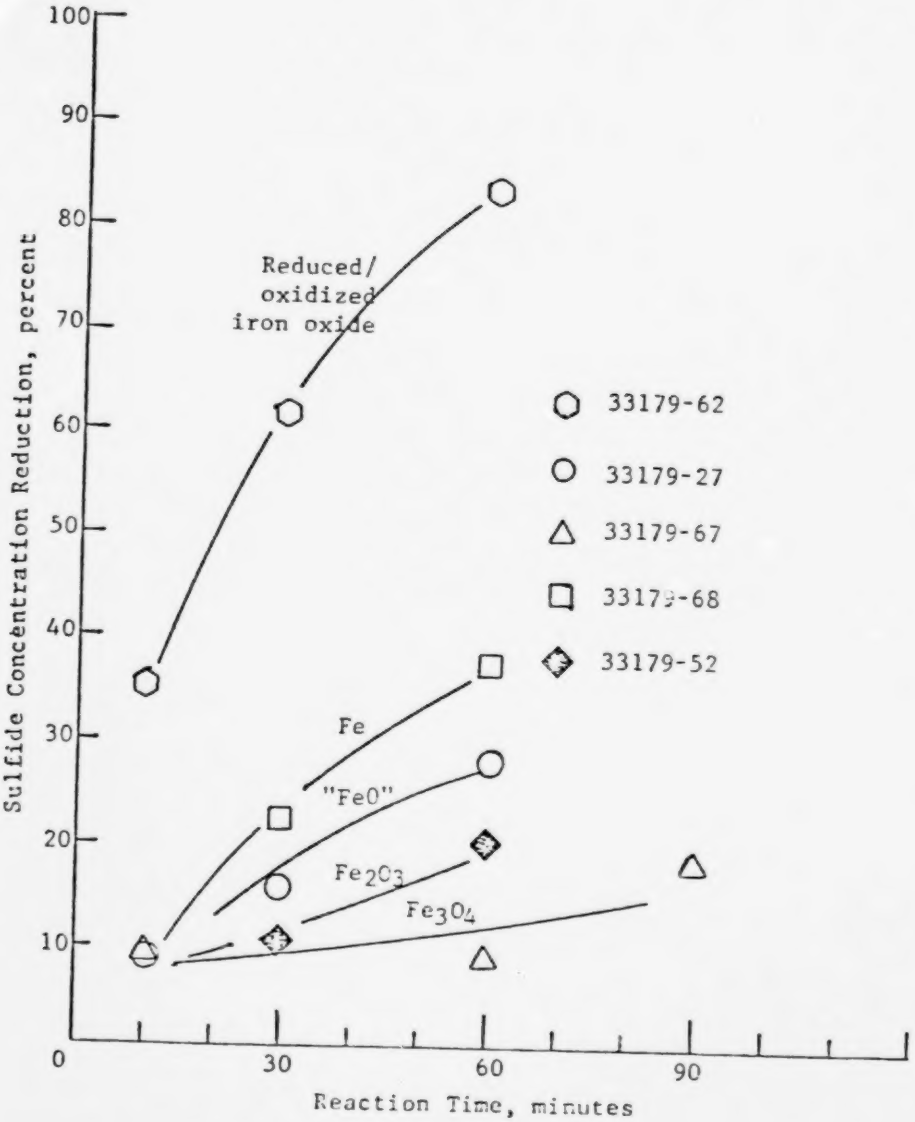

FIGURE 26. EFFECT OF VARIOUS FORMS OF IRON ON SULFIDE REDUCTION

These observations suggested that the activity of the reduced iron oxide/oxidized material may be due in part to ferrous/ferric hydroxide formed on the surface by reaction with the water in the spent leachant. Iron powder is known to react slowly with water to form $Fe(OH)_2$ according to the reaction $Fe + 2H_2O \rightarrow Fe^{++} + 2OH^- + H_2$, and similar but greater activity would be expected for an iron powder with a surface area great enough to make it pyrophoric in air. The fact that the spent leachant solution is alkaline might explain the low rate of activity observed. It also is known that specially prepared "FeO" is pyrophoric and reacts to decompose water. Such behavior could also supply the needed species for sulfide ion removal. "FeO" may be formed during the controlled exposure of the reduced iron oxide to air. A mechanism for sulfide removal that might explain the behavior of the active species is illustrated by the following set of chemical equations.

Active iron formation:

$$3H_2 + Fe_2O_3 = 2Fe + 3H_2O$$

$$Fe + \text{limited } O_2 = FeO \text{ (and unreacted Fe, } Fe_3O_4 \text{ and } Fe_2O_3)$$

(pyrophoric material)

$$3FeO + 5H_2O = Fe(OH)_2 + H_2 + 2Fe(OH)3$$

$$Fe + 2H_2O = Fe(OH)_2 + H_2$$

Desulfurization of leachant:

$$4S^= + 2Fe(OH)_2 + 2Fe(OH)_3 \rightarrow 2FeS + 2FeS(OH) + 8OH^-$$

Regeneration of the spent iron may require either oxidation of this type

$$2FeS + 2FeS(OH) + 6.5O_2 \rightarrow 4SO_2 + 2Fe_2O_3 + H_2O$$

or direct reduction of the spent reagent with hydrogen of this type

$$7H_2 + 2FeS + 2FeS(OH) + 2Fe_2O_3 \rightarrow 4S + 8H_2O + 8Fe.$$

Soluble Iron Compounds. On an exploratory basis, leachant desulfurization with the soluble iron compounds, sodium ferrite, and iron nitrates, was investigated. (See Appendix 3-E.)

The sodium ferrite was found to reduce sulfide sulfur concentrations effectively -- typically by 90 percent with fresh material, and by 80+ percent with recycled material. However, total sulfur concentrations remained high (e.g., 56 and 75 percent). In addition, the results of cursory cost evaluation indicated that cost of this method would be high.

Ferric nitrate also was found to reduce sulfide sulfur concentrations effectively. Total sulfur concentrations appeared to be reduced in a like manner. But here the results indicated that large proportions of iron were required for effective desulfurization. Hence, an economical method of recycling the iron values would be required to incorporate this approach in a viable commercial process.

Iron Carbonate. A potential method of leachant regeneration based on the use of iron carbonate was devised and evaluated. The leachant desulfurization step is illustrated by the following chemical equation:

$$\underline{\mathrm{FeCO_3}} + \mathrm{Na_2S} \qquad \underline{\mathrm{FeS}} + \mathrm{Na_2CO_3}.$$

A number of possible methods of regenerating iron carbonate for recycle from the ferrous sulfide were devised for screening:

- Sparging with carbon dioxide at atmospheric pressure and at 25 C to 80 C.
- Treatment with carbon dioxide in a pressure vessel at 150 to 600 psig and at 25 C to 180 C.
- Treatment with sodium carbonate solution, 10 percent to 20 percent by weight, and at 25 C to 100 C.
- Treatment with steam at 110 C to 150 C, to be followed by reaction of the hydrated oxide with sodium carbonate.

A preliminary flow sheet for leachant regeneration process using iron carbonate and recycling the iron values is given in Figure 27.

Recycle of Iron Values. Potential methods of recycling the iron values that are depicted by the following chemical reactions were screened.

(a) Carbon dioxide sparge

$$FeS + CO_2(150\text{-}600\text{ psi}) + H_2O \xrightarrow[25\text{-}180\text{ C}]{} FeCO_3 + H_2S\uparrow$$

(b) Carbon dioxide at elevated pressure and temperature

$$FeS + CO_2(150\text{-}600\text{ psi}) + H_2O \xrightarrow[25\text{-}180\text{ C}]{} FeCO_3 + H_2S\uparrow$$

(c) Sodium carbonate or bicarbonate solution

$$FeS + Na_2CO_3 + 2H_2O \xrightarrow[25\text{-}100\text{ C}]{} \underline{FeCO_3} + H_2S\uparrow + NaOH$$

or

$$FeS + NaHCO_3 + H_2O \xrightarrow[25\text{-}100\text{ C}]{} \underline{FeCO_3} + H_2S\uparrow + NaOH$$

(d) Steam, then sodium carbonate

$$FeS + \text{steam} \xrightarrow[110\text{-}150\text{ C}]{} \underline{FeO \cdot H_2O} + H_2S\uparrow$$

$$FeO \cdot H_2O + Na_2CO_3 \longrightarrow \underline{FeCO_3} + 2NaOH$$

(e) Steam and carbon dioxide

$$FeS + CO_2 + \text{steam} \longrightarrow FeCO_3 + H_2S\uparrow$$

(f) Oxygen, then sodium carbonate

$$FeS + H_2O + O_2 \longrightarrow FeSO_4$$

$$FeSO_4 + Na_2CO_3 \longrightarrow FeCO_3 + Na_2SO_4$$

$$Na_2SO_4 + CaO \longrightarrow CaSO_4 + 2NaOH$$

(g) Sulfuric acid, then sodium carbonate

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S\uparrow$$

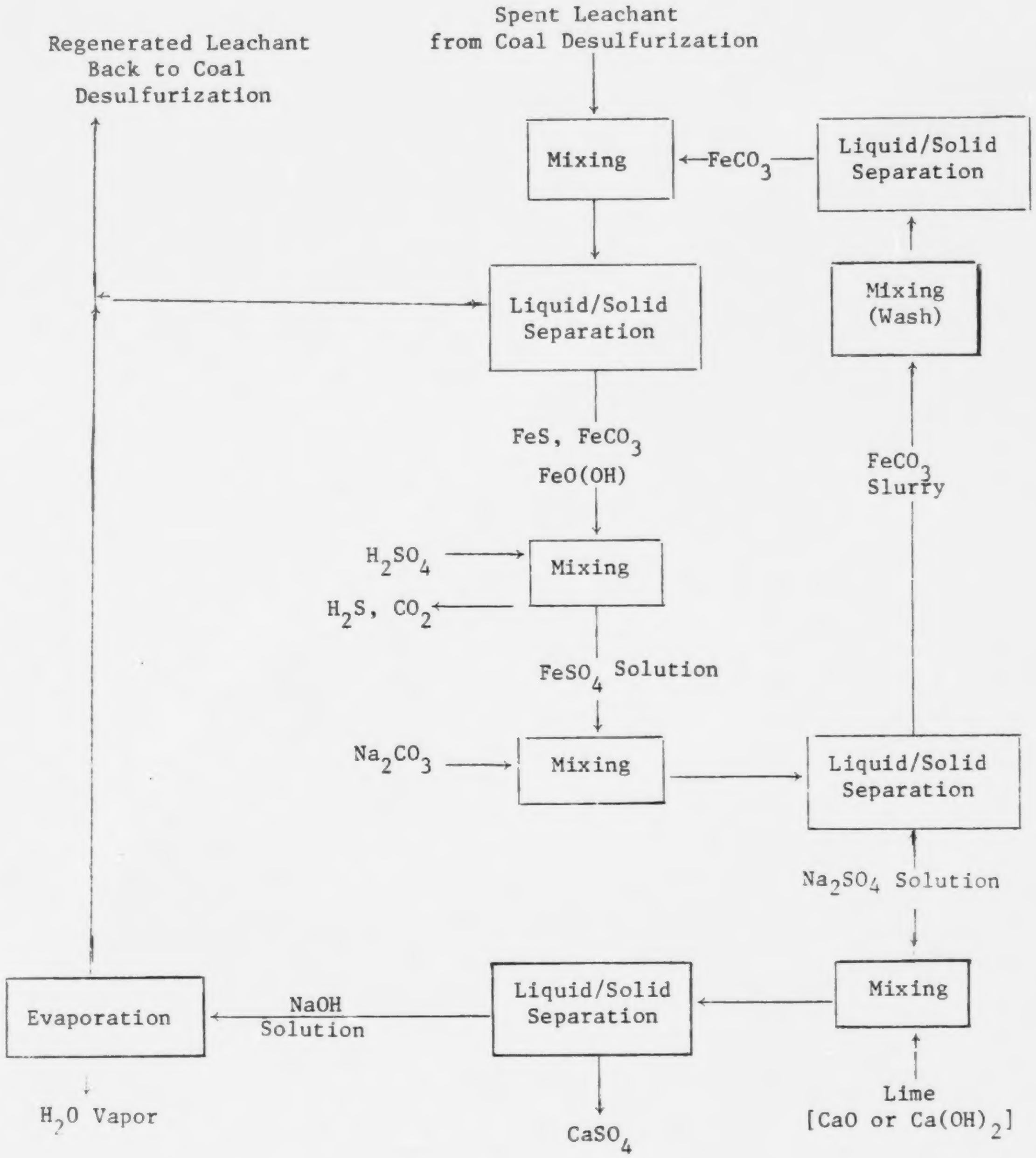
Spent Leachant from Coal Desulfurization
Regenerated Leachant Back to Coal Desulfurization
Mixing
FeCO3
Liquid/Solid Separation
Liquid/Solid Separation
Mixing (Wash)
FeS, FeCO3 FeO(OH)
FeCO3 Slurry
H2SO4
Mixing
H2S, CO2
FeSO4 Solution
Na2CO3
Mixing
Liquid/Solid Separation
Na2SO4 Solution
Evaporation
NaOH Solution
Liquid/Solid Separation
Mixing
H2O Vapor
CaSO4
Lime [CaO or Ca(OH)2]

FIGURE 27. FLOW SHEET FOR LEACHANT REGENERATION WITH IRON CARBONATE

$$FeSO_4 + Na_2CO_3 \longrightarrow \underline{FeCO_3} + Na_2SO_4$$

$$Na_2SO_4 + CaO \longrightarrow CaSO_4 + 2NaOH\ .$$

In the investigation of these reactions, inert atmospheres were employed and, in most of the reactions in aqueous liquid, metallic iron was introduced to suppress ferric ion concentrations.

Observation of exploratory experiments indicated that some ferrous sulfide can be converted to ferrous carbonate by Reactions (a) and (b). Hydrogen sulfide was evolved when a slurry of ferrous sulfide was sparged with carbon dioxide. Treatment of ferrous sulfide slurry with carbon dioxide at elevated temperature and pressure in an autoclave yielded a product that copiously evolved an odorless (CO_2) gas when acidified. However, kinetics of the reactions were poor, and these methods probably are not acceptable for a commercial process.

The Reactions of (c) -- the conversion of iron sulfide with bicarbonate or carbonate -- were calculated to have small, but negative free energy changes when all reactants and products were assumed to be in the standard states ($\Delta F \sim 3{,}600$ Cal/mole). However, under the indicated reaction conditions, no evolution of hydrogen sulfide was detected.

Although it has been reported by others that steam reacts with FeS to produce hydrogen sulfide and hydrated iron oxide, no evolution of hydrogen sulfide was detected in our experiments with either Reactions (d) or (e).

Thus, among the seven methods, as they were carried out in the exploratory screening experiments, only Reactions (b), (f) and (g) gave positive results. In the two experiments with Reaction (b), temperature and pressure were increased slowly in the ranges indicated, then were held at the maximum values for 2-1/2 and 3 hours. Gases in the pressure vessel were vented slowly (additional carbon dioxide was introduced to compensate for the loss) and were checked for H_2S content. Hydrogen sulfide was found to be evolved in significant concentrations only at temperatures and pressures near the maxima indicated. The resulting solid material was the expected greenish-grey material that, when treated with dilute hydrochloric acid, was found to copiously evolve an odorless gas which was concluded to be carbon dioxide.

The first step in Reaction (f), the oxidation of iron sulfide to iron sulfate, has been demonstrated in previous work on this project and is,in fact, the reaction that produces acid mine waters. Thus, experiments were carried out only on the precipitation of iron carbonate from the sulfate solution. Results were positive, yielding the expected grey precipitate when air (oxygen) was excluded from the reaction vessels. The sodium sulfate solution which results can then be treated with lime to reclaim the sodium values as the hydroxide and to produce a nonpolluting calcium sulfate solid for discard or utilization. The reactions outlined for Reaction (g) likewise yielded a product which tests indicated was iron carbonate.

Results of the experiments that have been discussed and summarized in Table 3.17 have shown the iron carbonate recycled by Reaction (g) to be very effective for leachant desulfurization.

Leachant Regeneration with Activated Carbon

Effective adsorption of sulfide sulfur (95-98 percent) was obtained by passing leachant solution through a column of activated carbon.

Adsorption of sodium on the column was indicated to be low. However, oxidized sulfur species (e.g., thiosulfate, sulfite, sulfate) were not adsorbed effectively, and the capacity of the carbon for sulfide adsorption was extremely low. In addition, polysulfides were formed.

No work was done on desorption of sulfide from the column.

Leachant Regeneration by Electrolysis

Electrolysis, which has the potential for very low cost leachant desulfurization, was investigated using two systems: the tripolar wiped electrode system and an iron-screen anode system.

Sulfide extractions were low -- in the range of 31 to 54 percent. Total sulfur checks made in the screen-anode work showed that total sulfur concentrations remained high, presumably due to the formation of oxysulfur anions (thiosulfate, sulfite, sulfate).

This approach may have potential, but a sizeable effort appears necessary.

Leachant Regeneration With Lime

In view of the considerable cost advantage that could be realized if leachant desulfurization could be carried out using lime, several experiments were run to check the chemical reactions involved under selected regeneration conditions.

Direct regeneration of leachant with lime is based on oxidation of the sulfur species to sulfate, which would then be precipitated as calcium sulfate.

Results of the experiments showed no precipitation of sulfate, presumably because the solubility of calcium hydroxide was lower than that of calcium sulfate under all sets of conditions.

Leachant Regeneration With Copper

Copper is another common metal that forms insoluble sulfides. The copper sulfides are, in fact, much less soluble than the zinc compounds. Copper also can be taken into solution as the copper/ammonia complex, and the metal can be regenerated from the sulfide under moderate conditions.

The results of several experiments with soluble copper confirmed that up to 90 percent of the sulfide sulfur can be extracted from coal leachant. However, less than half of the total sulfur was precipitated -- presumably because of reactions that form oxysulfur anions.

Because of this result and overall cost considerations, further work on the approach was abandoned.

Coal Desulfurization

The objective of this work was to develop "near-optimum" desulfurization processing parameters for:

- Northern Appalachian coal from the Homer City coal-cleaning facility
- Midwestern coal (an Illinois No. 6 coal from the Delta Mine, Williamson County, Seam 6)
- Western coal (a subbituminous B coal from the Colstrip Mine, Rosebud County.

Since each coal is different in terms of rank, composition, and distribution of mineral matter in coal matrix, processing conditions were varied to achieve maximum desulfurization and minimum coal solubilization. Both hydrothermal treatment and oxidative desulfurization studies were conducted.

Hydrothermal Treatment. The processing conditions used for hydrothermal treatment, depending on the coal, were:

1. Leachants
    - (a) Aqueous mixture of NaOH and CaO
    - (b) Aqueous solution of Na_2CO_3
    - (c) Water alone
2. Temperature -- 225 to 300 C
3. Pressure -- 1000 psig
4. Time -- 10 to 60 min.
5. Particle size of coal -- 100 percent -8 mesh and 100 percent -50 mesh.

The operating procedure entailed heating an aqueous slurry of the coal and leachant in the autoclave at a specified temperature and withdrawing samples at specified intervals. The treated coal was then separated from the spent leachant by a series of washing and filtration operations and vacuum dried for analysis. In some cases, the washed desulfurized coal was separated into various size fractions by screening before drying.

Treatment conditions for each of the coals and analytical data are shown in Tables 34, 35, and 36.

The Homer City caol was found to be subject to desulfurization and demineralization by treatment with the mixed leachant and water alone (Table 34). Treatment with the mixed leachant resulted in the extraction of 65 percent of the total sulfur (94 percent of the pyritic sulfur) in 10 minutes at 275 C (Experiment 33821-95-1).

After hydrothermal treatment the coal can be separated into various size distributions for evaluation (Experiments 33821-95-6, -7, and -10). The results in Table 34 indicate that the mineral matter content of the coal in the plus 200 mesh size fraction contains approximately 7 to 8 weight percent ash. The major portion of the ash is contained in the minus 325 mesh fraction. A large proportion of the ash in the minus 325 mesh material is sodium and calcium compounds. Previous Battelle work has shown that this high content can be substantially reduced by a weak acid wash.

TABLE 34. HYDROTHERMAL TREATMENT OF NORTHERN APPALACHIAN (HOMER CITY) COAL

Sample/ Run No. 33821-	Particle Size Distribution		Reaction Conditions				
	Mesh Size	Percent Distribution	Water/ Coal	NaOH/ Coal	CaO/ Coal	Temp, C	Time, min
98 (Raw coal)(a)	8 x 0	100					
98-1 (Raw coal)	8 x 100	74	--	--	--	--	--
98-2 "	100 x 200	7(b)	--	--	--	--	--
98-5 "	- 325	16	--	--	--	--	--
95-1 (Clean coal)	8 x 0	100	3	.26	.10	275	10
95-2 (Clean coal)	8 x 0	100	3	.26	.10	275	
95-6(c) (Clean coal)	8 x 100	33	3	.26	.[illegible]	275	
95-7 (Clean coal)	100 x 200	12	3	.26	.10	275	
95-10 (Clean coal)	325 x 0	51	3	.26	.10	--	--

Sample Run No. 33821-	Particle Size Distribution		Analysis, wt %							
					Sulfur (MAF)					
	Mesh Size	Percent Distribution	Ash (MF)	H_2O	Total	Pyritic	Sulfate	Organic	(MAF)	(MAF)
98 (Raw coal(a)	8 x 0	100	20.2	--	2.82	2.60	--	--	--	--
98-1 "	8x100	74	21.3	.12	3.02	3.01	.06	NA	--	--
98-2 "	100x200	7(b)	12.4	.59	2.21	1.62	.06	.53	--	--
98-5 "	325 x 0	16	22.1	.04	2.67	1.63	.37	.67	--	--
95-1 (Clean coal)	8 x 0	100	20.4	.10	.91	.14	.13	.64	1.25	5.46
95-2 "	8 x 0	100	21.9	.17	1.04	.19	.17	.68	1.58	5.21
95-6(c)"	+100	33	8.4	.29	.81	.15	.08	.58	1.24	.59
95-7 "	100x200	12	7.4	.62	.74	.02	.07	.65	1.10	.74
95-10 "	325 x 0	51	50.0	.37	1.08	.66	.40	NA	4.12	23.2

(a) A sample of raw coal from Run 98 separated by screening into various size fractions.

(b) 3 percent 200 x 325 mesh.

(c) Bulk sample from Experiment 95-2 washed to remove spent leachant and then separated into various size fractions by screening.

TABLE 35. HYDROTHERMAL TREATMENT OF SUBBITUMINOUS WESTERN COAL

Sample/ Run No. 33821-	Particle Size Distribution		Reaction Conditions					
	Mesh Size	Percent	Water/ Coal	NaOH/ Coal	CaO/ Coal	Na_2CO_3/ Coal	Temp, C	Time, min
88-1 (Raw Coal)	50 x 0	100	--	--	--	---	--	--
91-1	50 x 0	100	3	.03	.10	--	225	60
91-3[a]	50 x 0	100	3	.03	.10	--	225	60
93-1	50 x 0	100	3	.03	.10	--	225	15
93-4[b]	50 x 70	16	3	.03	.10	--	225	60
93-5	70 x 200	53	3	.03	.10	--	225	"
93-6	200x270	6	3	.03	.10	--	225	"
93-7	270x325	2	3	.03	.10	--	225	"
93-8	-325	21	3	.03	.10	--	225	"
93-Composite[c]	50 x 0	100						
97-1[b]	+100	52	3	--	--	--	275	10
97-2	100x200	26	3	--	--	--	275	"
97-3	200x270	2	3	--	--	--	275	"
97-4	270x325	2	3	--	--	--	275	"
97-5	325 x 0	18	3	--	--	--	275	"
97-Composite[c]	50 x 0	100						
96-1	50 x 0	100	3	--	--	.06	275	10
96-2	50 x 0	100	3	--	--	.06	275	20

Sample/ Run No. 33821-	Particle Size Distrib.									
	Mesh Size	Percent	Ash (MF)	H_2O	Total	Pyritic	Sulfate	Organic	Na (MAF)	Ca (MAF)
88-1 (Raw Coal)	50 x 0	100	10.3	15.0	.92	0.26	0.17	0.49	--	--
91-1	50 x 0	100	12.3	16.8	.83	.32	.04	.47	.97	6.93
91-3[a]	50 x 0	100	23.6	1.50	.92	.31	.07	.54	1.00	11.2
93-1	50 x 0	100	16.7	4.00	.66	.18	.03	.46	.25	6.26
93-4[b]	50 x 70	16	15.4	3.61	.55	.18	.01	.36	.67	7.23
93-5	65x200	53	15.4	4.23	.64	.32	.02	.30	.59	6.56
93-6	200x270	6	17.4	4.00	.74	.25	.04	.45	.43	8.06
93-7	270x325	2	16.8	4.10	.69	.23	.04	.43	.45	7.72
93-8	325 x 0	21	33.4	3.74	.70	.22	.14	.34	.61	21.2
93-Composite[c]	50 x 0	100	19.0	3.32	.70	.26	.04	.32		
97-1[b]	50 x 100	52	8.1	1.43	.57	.10	.01	.46	NA	NA
97-2	100x200	26	9.1	1.38	.61	.17	.02	.42	NA	NA
97-3	200x270	2	(d)	(d)	NA	NA	NA	NA	NA	NA
97.4	270x325	2	(d)	(d)	NA	NA	NA	NA	NA	NA
97-5	325 x 0	18	15.5	1.50	.90	.37	.07	.46	--	--
97-Composite[c]	50 x 0	100	9.36	1.37	.64	.16	.02	.43	NA	NA
96-1	50 x 0	100	11.2	3.38	.67	.17	.01	.49	.65	1.74
96-2	50 x 0	100	11.0	3.39	.67	.17	.01	.49	.65	1.57

(a) Crust formed on filter, washed, dried, and analyzed separately.

(b) Cleaned coal separated in various size fractions after weaning to remove spent leachant.

(c) Composite analysis of screened fractions.

(d) Sample too small to measure

On the basis of these data, the high-sulfur, middling-product from the Homer City coal-cleaning facility can be chemically cleaned to produce a moderate mineral matter coal with a sulfur content less than the 1971 sulfur emission standards for new sources (1.2 lb $SO_2/10^6$ Btu).

Similar results were obtained with the Western subbituminous coal from the Colstrip Mine (Table 35). As mined, this coal will not meet the 1971 sulfur emission standard. However, treatment with water, Na_2CO_3, or a mixture of NaOH and CaO at temperatures ranging from 225 to 275 C resulted in extraction of a portion of the pyritic sulfur to produce a coal product having a sulfur content equivalent to less than 1.2 lb/10^6 Btu.

In other work supported by Battelle, a coal product was produced from a similar subbituminous Western coal having a sulfur content equivalent to 0.31 lb $SO_2/10^6$ Btu.

Separation of the mineral matter from the cleaned coal by physical beneficiation (washing) was not as evident with the Western coal as with the northern Appalachian coal. However, preliminary results (Experiments 33821-97-1 through -5) indicate that this approach could be feasible.

The Midwest coal from Delta Mine (Table 36) represents a high pyritic and high organic sulfur coal. Treating this coal at 275 C to 300 C for 10 minutes with the mixed leachant resulted in the extraction of approximately 64 percent of the total sulfur. Degrees of extraction of the pyritic, sulfate, and organic sulfur were approximately 91, 83, and 20 percent, respectively.

As such, this coal product will not meet sulfur emission standards for new sources. However, the alkali left in the coal will act as a sulfur getter during combustion. Therefore, it should be possible to burn this treated coal with little or no sulfur emission.

Oxidative Desulfurization. Oxidative leaching, using low concentrations of sodium hydroxide and moderate temperatures, offers the potential advantages of low processing costs, low sodium incorporation, relative ease of leachant regeneration, and potentially high product yields. In addition, oxidation processes have been reported to reduce organic sulfur concentrations.

A debt fraction of 0.6 is assumed for the plant. This fraction implies that 60 percent of the capital is borrowed for plant construction and startup. This assumption is also consonant with a large investor borrowing the funds.

The plant economic life is assumed to be 12 years, construction requiring an additional 3 years. During the three construction years, capital is assumed to be spent in a 20-40-40 percent pattern. When combined with the debt on the plant, and the assumed interest rate, the plant will then owe 120 percent of the capital cost on opening day. Add to this an 8 percent working capital assumption, and the total debt on opening day is 128 percent.

For simplification, during the 15 years of operation and construction, inflation is neglected. The annual income from operations is assumed to be 20 percent before income taxes and interest, and to be constant throughout the economic life of the plant. The capital-related costs, including depreciation, maintenance, property and ad valorem taxes, and inventory taxes, is assumed to be 21 percent of all invested capital.

The assumptions regarding capital are probably the most critical factor in cost for the process, as they affect the final cost of coal, which in turn affects the cost of using treated coal in the process and the cost of the product coal inventory.

In later cases, such as the Westland Coal Case, the cost of coal treatment is shown to be $37.60, of which $20.72 represents capital-related charges. By changing the income from operations by 5 percent, $2.00 can be saved on the profit, taxes, and interest for each ton of coal. This $2.00 is reflected as a decrease in treated coal costs in the process cost section, about $0.60 in working capital related charges, and $0.14 in moisture penalty costs. The original decrease of $2.00 is then magnified to about $3.00 in savings for the process costs, which is 8 percent of the total processing costs. It follows that comparison of the hydrothermal process treatment costs with costs of other processes without close scrutiny of the underlying economic assumptions could result in erroneous conclusions. In fact, by eliminating all associated profit, as is frequently done with flue gas desulfurization, the economics of the Westland Coal Case are reduced by almost 20 percent.

The working capital in each case is based on the assumptions in Table 38. If working capital were increased to include coal holdings, the required capital would have to be increased by $2.5 million for inventory and $4.8 million for receivables less the payables at $20/ton of coal.

Raw materials cost assumptions are listed in Table 39. These costs are generalized from the January - March, 1978 Chemical Market Reporter. Coal costs are not taken from any single source, but are based on generalized observation of the market.

Capital equipment costs were derived from several sources, predominantly References 5 through 7. When earlier estimates of equipment were considered appropriate, these estimates were included and escalated to the January - March, 1978 timeframe. When estimates from the references were used, these data were escalated to the 1978 basic also, using the mining and milling section of the M & S equipment cost index. Labor estimates are based on $16.00/hour, which includes supervision and other related items.

Summary

Three case studies were conducted to derive cost estimates with the following results and conclusions.

Hydrothermal process conditions for desulfurization of each of the coals are as follows:

These conditions were determined by desulfurization tests on these particular coals and from other related desulfurization work conducted at Battelle on the desulfurization of a wide variety of coals.

Coal	Westland	Colstrip	Homer City
Particle Size, Mesh	50 x 0	50 x 0	50 x 0
Temperature, °C	527°F (275°C)	527°F (275°C)	527°F (275°C)
Pressure, psig	1000	1000	1000
Time, min.	10	10	10
Leachant Ratio			
Coal/Na/Ca/H_2O	1/0.16/0.05/2	1/0/0/2*	1/0.16/0.05/2

Only water used as leachant

Westland Coal Processing

The hydrothermal processing of Westland coal using HTT is typical of Eastern coal treatment and is considered to be the case with the least environmental impact with zero liquid discharge. The economics of the process would require a coal cleaning charge of $37.00 to $38.00 for each ton of coal. This cost would be added to the raw coal purchase price. Process costs are expected to continue to increase due to inflation and increasing interest rates. Some process modifications and improvements can be realized by eliminating nickel in the reactor and fire-heater heat exchangers, The ferrous carbonate system could still potentially reduce the cost of processing, although the reduction at this point is not thought to be large unless the $FeCO_3$ to $S^=$ ratio can be reduced. Another alternative, which should be explored, is to add a sulfuric acid plant instead of a sulfur plant. However, this alternative must be investigated in detail since H_2S feed purification would be required to make the plant economically viable.

Colstrip Coal Processing

The Colstrip case is typical of Western subbituminous treatment. Only water and a dispersant for raw chemicals are used to treat the coal rather than a true leachant. Total estimated cost of a ton of clean coal in this case, exclusive of transportation, is $18.97.

Some concepts that merit further investigation for this case are: running the solids countercurrent to the liquid in the reactor section as a countercurrent two-stage reactor to increase the untreated water recycle; investigating hydroclones for solid/liquid separation to achieve better dewatering; and recovery of metals in the throwaway stream, since rare earth metals, such as vanadium, are present in the coal, and are presumed to leach out of the coal.

TABLE 38. ASSUMPTIONS OF WORKING CAPITAL REQUIREMENTS

30 day average inventory of raw materials on hand at all times

15 days average product inventory on hand at all times

40 days of receivables outstanding at all times

15 days payables outstanding

No raw coal cost is assessed to product or raw material inventories (Coal is treated on a toll basis)

$$\text{Working Capital} = \text{Product Inventory Costs} + \text{Raw Materials Inventory} + \text{Receivables} - \text{Payables}$$

TABLE 39. RAW MATERIALS COSTS[(a)]

Material (All Commercial Grade)	Cost
Sodium Hydroxide	$160.00/Ton
Lime	28.00/Ton
Sodium Carbonate	56.00/Ton
Sulfur	40.00/Ton
Ferrous Sulfate	53.00/Ton
Electricity	0.035/Kwh
Process Water	$0.50/10^3$ Gal
Cooling Water	$0.50/10^3$ Gal
Sulfuric Acid	53.00/Ton
Landfill Costs	3.00/Ton
Coal(b)	
Westland	20.00/Ton
Colstrip	8.75/Ton
Homer City	13.00/Ton

(a) Chemical Market Reporter, period December, 1977 - March, 1978.

(b) General market observations.

Homer City Coal (Physical/Hydrothermal Treatment)

In this case, the existing physical cleaning process for this Western Pennsylvania coal is combined with a hydrothermal treatment process essentially identical to that used with Westland coal. The estimated cost of the combined physical/HTT treated coal is $24.14. Elimination of the middle fraction dryers in the physical cleaning process could reduce this cost. Process modifications recommended in the Westland case would also be applicable here.

RESULTS AND DISCUSSION

In the following discussion, the processes, material balances, alternatives, and process economics for each of the three cases are described.

Westland Coal

The Westland Coal Case is considered to be typical of Eastern coal treatment. The case is generally typified by essentially zero liquid discharge, the only requirements in this area being sanitary sewerage and removal of the entrained sulfur compounds as elemental sulfur. This case is considered the one with the least environmental impact.

The treatment summary is shown in Table 40 with the influent and effluent coal consistency tabulated. Sulfur decrease is significant, as is nonsodium and noncalcium related ash.

The water increase of the treated coal requires that a penalty for firing of excess coal be included. This penalty is included in the price of the coal in the solid/liquid separation section.

Process Description. A block diagram of the process is shown in Figure 28, with Figures 29 and 30 showing details of the hydrothermal, solid/liquid separation, and regeneration sections, respectively.

Hydrothermal Treatment. The coal is metered into the hydrothermal plant section, where it is mixed with the makeup sodium hydroxide, slaked lime, and the regenerated leachant in a ratio of 1 part coal to 0.16/0.05/2 sodium/calcium/water. The leachant is then heated to 527 F and pressurized to 1000 psig and fed to a continuous flow autoclave. The solution in the autoclave is held for an average of 10 minutes and then cooled and depressurized. The steam resulting from depressurization is used in the washing section to maintain temperatures.

Solid Liquid Separation. The treated slurry is then transported to the solid/liquid separation section. Here it is washed countercurrently at 1.75/1 saturated lime water to coal. Washing is done in stages, with four disk filters, eight belt filters, and a screen bowl centrifuge. The treated coal is passed on to storage at 42 percent moisture, and the leachant and washwater are passed to a six effect, backware feed evaporator. The excess water is removed from the leachant and added to the wash tank.

TABLE 40. WESTLAND COAL TREATMENT SUMMARY

	Raw Coal, percent	Treated Coal, percent
Coal Solids (MAF)[(a)]	97.92	99.14
Sulfur (MAF)	2.08	0.86
Ash (MF)[(b)]	7.96	7.88
Na (MF)[(c)]	0.02	0.43
Ca (MF)[(c)]	0.07	2.65
Water	5.00	42.00

[(a)] MAF: Moisture and ash free basis

[(b)] MF: Moisture free basis

[(c)] Contained in ash.

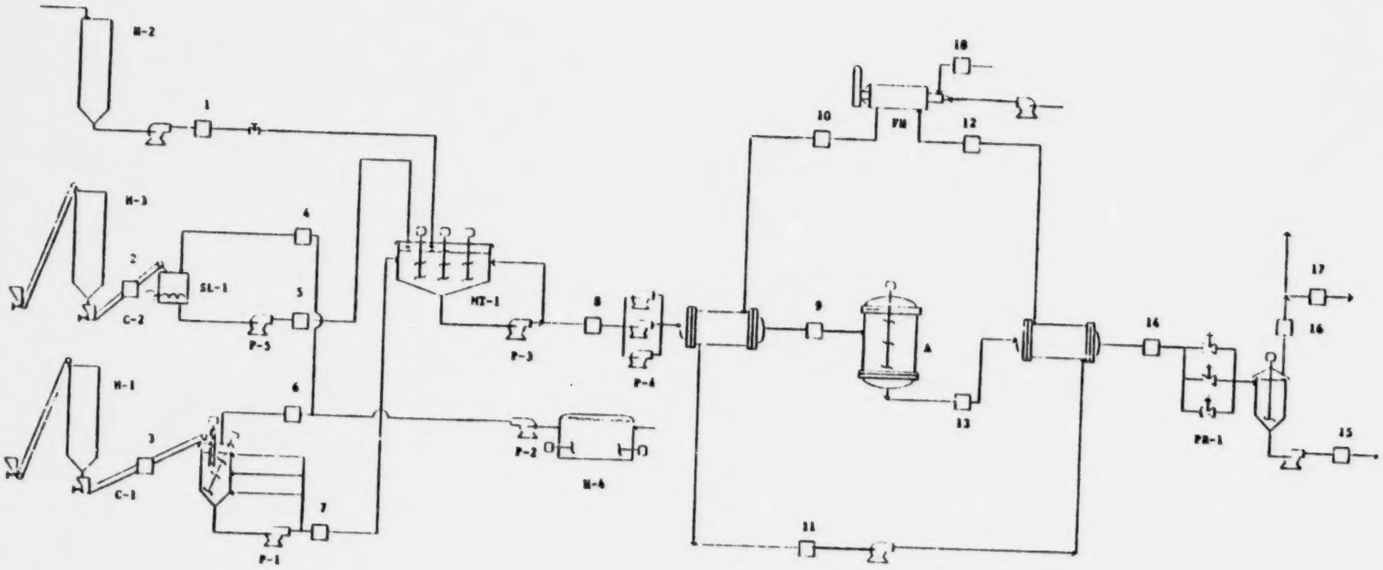
H-2
1
H-3
2
SL-1
4
5
C-2
P-5
H-1
3
C-1
6
7
P-1
MT-1
P-3
8
P-4
P-2
H-4
10
FM
18
12
9
A
13
11
14
PR-1
17
16
15

FIGURE 28. HYDROTHERMAL TREATMENT SECTION FOR WESTLAND COAL

(See Table 42 for material and energy balances at numbered locations and Table 47 for equipment list and description.)

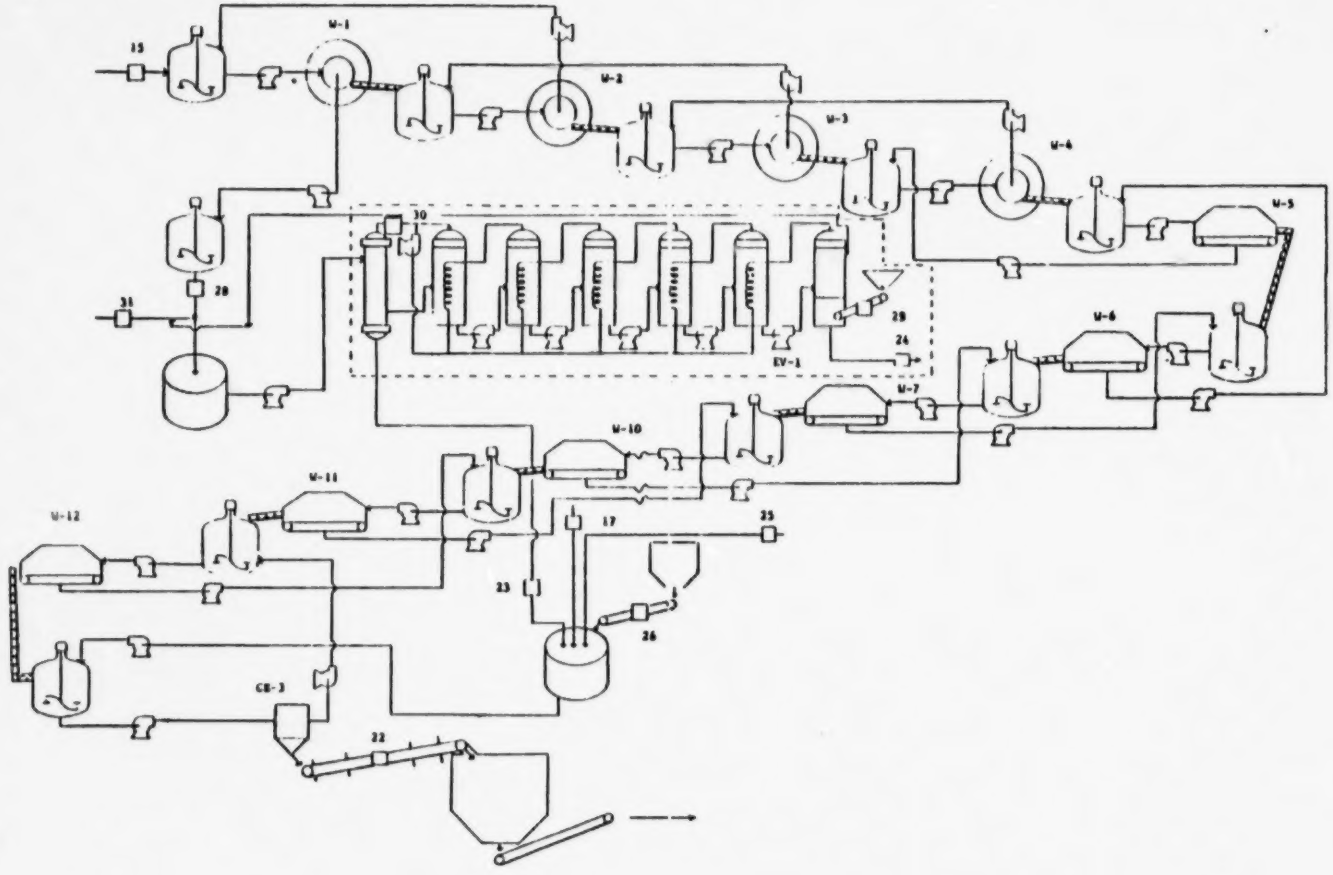
15
W-1
W-2
W-3
W-4
W-5
W-6
W-7
W-10
W-11
W-12
30
31
20
29
24
EV-1
17
25
23
26
CB-3
22

FIGURE 29. SOLID/LIQUID SEPARATION SECTION FOR WESTLAND COAL

(See Table 43 for material and energy balance at numbered location and Table 48 for equipment list and description.)

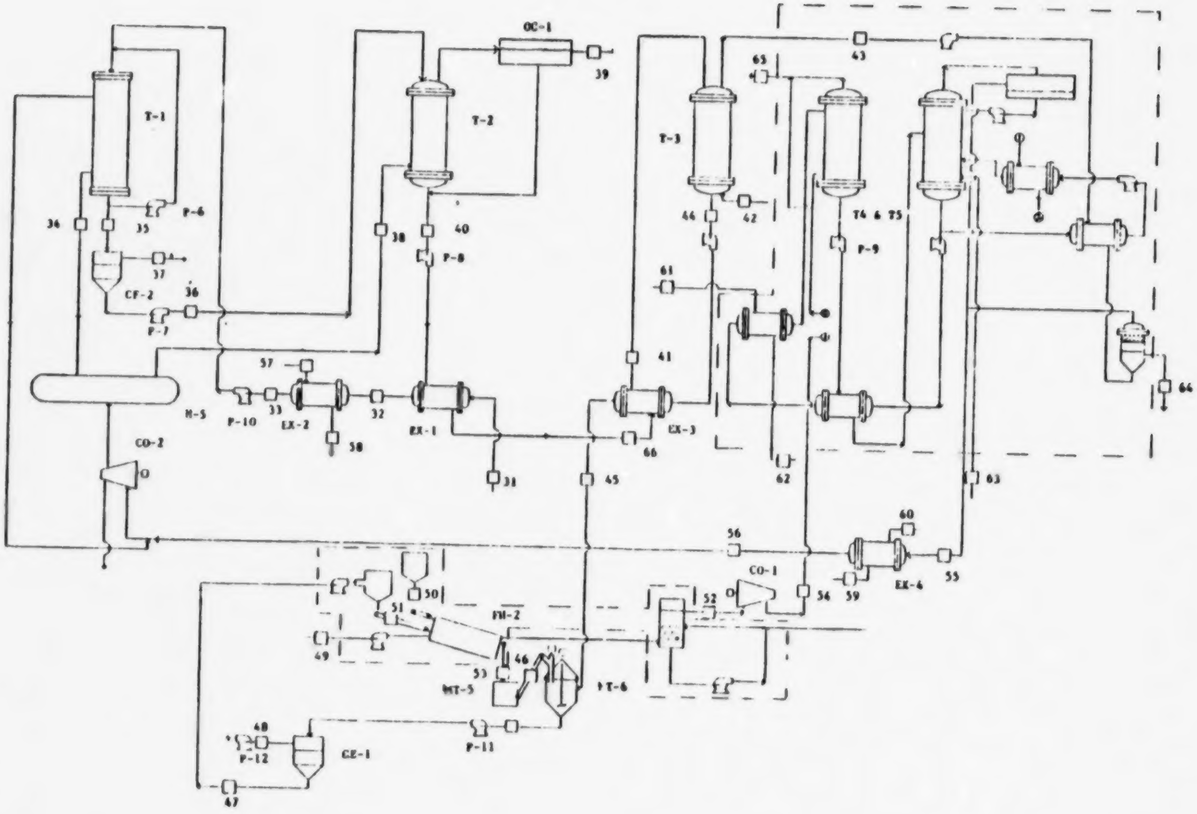
T-1
P-6
34
35
CF-2
37
36
P-7
M-5
CO-2
P-10
33
EX-2
57
58
32
EX-1
31
T-2
38
40
P-8
OC-1
39
T-3
44
42
41
EX-3
66
45
61
65
43
T4 & T5
P-9
62
63
64
60
EX-4
55
56
59
54
CO-1
52
50
51
FM-2
49
46
53
MT-5
FT-6
48
P-12
CE-1
P-11
47

FIGURE 30. CO_2 REGENERATION PROCESS FOR THE SPENT LEACHANT FROM WESTLAND COAL PROCESSING

(See Table 44 for material and energy balance at numbered location and Table 49 for equipment list and description.)

Regeneration. The spent leachant is then pumped into the regeneration section. In Tower T-1 (Figure 30) it is carbonated to prevent foaming. It is then removed and centrifuged. A mixture of ash and calcium carbonate carbonate is removed for landfill.

The centrifuged leachant is then passed to T-2, where carbon dioxide drives off the sulfur as hydrogen sulfide gas. This gas, a carbon dioxide and H_2S mixture saturated with water, is compressed slightly and sent to a Claus plant for treatment (not shown). The Claus plant tailgas is treated in a Stretford plant, and finally exhausted to the atmosphere. Pure sulfur is shipped to storage.

The highly carbonated liquor from Tower T-2 is steam stripped to Tower T-3 to remove some of the carbon dioxide. This gas from T-3 is blended with the exit gas from Tower T-5. The liquor from T-3 is cooled by countercurrent exchange with the feed to Tower T-3, and treated with lime to precipitate the remaining carbonate. This regenerated leachant is then pumped to storage pending reuse.

The calcium carbonate precipitated by the lime addition is roasted in a kiln to release the carbon dioxide and the calcium oxide is recycled for leachant regeneration.

The kiln uses raw coal as a heat source for decarbonation of the precipitate. Its stack gas is cooled to about 500 F in a dew point control scrubber, used as a heat source for T-5, and then scrubbed in T-4 to remove the SO_2 and CO_2, the SO_2 being converted to H_2S_x by the monoethanolamine scrubber solution. The treated gas is then released to the atmosphere.

Next, the monoethanolamine (MEA) is transferred to T-5, where the carbon dioxide and hydrogen sulfide are desorbed, before the MEA is returned to the gas absorber.

From T-5, the carbon dioxide and hydrogen sulfide gas are mixed with the effluent from the steam stripper (Tower T-3) and the hot gases are cooled in a gas cooler. The gas bleed from the precarbonation tower is also mixed with the cooled gases. These gases are compressed, recooled, and transported to storage.

Based on experimental data from the 1975 Summary Report$^{(5)}$, the buildup of chloride and thiosulfate anions appears virtually nonexistent.

TABLE 43. WESTLAND COAL CASE SOLID LIQUID SEPARATION SECTION MATERIAL AND ENERGY BALANCE

Major Compounds	22	23	24	25	26	27	28	29	30	31
Coal Solids	52.9						0.2	52.9		0.3
Sulfur	0.5						0.3	0.5		0.5
Ash	4.6		100		100	0.1	6.9	4.6		10.2
Sodium	0.9						2.4	0.9		3.5
Calcium	0.3				54.1	0.1	1.1	0.3		1.6
Water	42.0	100		100		99.9	92.6	42.0	100	89.0
Total Flow	645 t/hr	680 gpm	0.736+/hr	1040 gpm	1.05 gpm	2798 t/hr	4977 gpm	16.0 t/hr	1750 gpm	3231 gpm
Temperature, F	192	212	300	60	70	180	180	70	212	210

TABLE 44. WESTLAND COAL CASE CO_2 REGENERATION SECTION MATERIAL AND ENERGY BALANCE

Major Compounds	Location in Figure 30											
	32	33	34	35	36	37	38	39	40	41	42	43
Coal Solids	0.3	0.3		0.3	0.1	5.3			0.1	0.1		
Sulfur	0.5	0.5		0.5	0.5		0.4	7.5				
Ash	10.2	10.2		14.3	11.6	73.8			15.9	15.9		
Sodium	3.5	3.5		3.4	3.5				33.5	33.5		
Calcium	1.6	1.6		1.5		35.2						
Water	89.0	89.0		84.9	87.8	21.0			84.0	84.0	100	65.0
Carbon Dioxide			100			27.1	99.6	92.5				35.0
Total Flow	3231 gpm	3231 gpm	86,900 lb/hr	3231 gpm	3197 gpm	40.28 t/hr	193,200 lb/hr	66.2 t/hr	3197 gpm	3197 gpm	121,520 lb/hr	186,944 lb/hr
Temperature, F	155	80	80	80	80	80	80	116	116	92	250	212

TABLE 44. (Continued)

Major Compounds	44	45	46	47	48	49	50	51	52	53	54	55
Coal Solids	0.1	0.1			0.1		85.8		0.1			
Sulfur							1.7				0.1	0.5
Ash	13.0	13.0	100	100	6.5		7.6	100		100		
Sodium	3.5	3.5	54.1	26.0	3.7							
Calcium								40.0		68.5		
Water	86.9	86.9			93.4		4.9		0.4		0.4	
Carbon Dioxide									33.7		33.7	99.5
Nitrogen						77.4			64.1		64.1	
Oxygen						22.6			1.7		1.7	
Total Flow	3197 gpm	3.97 gpm	44.7 t/hr	123 t/hr	3197 gpm	127,188 scfm	25.4 t/hr	79.9 t/hr	280,400 acfm	46.7 t/hr	249,790 acfm	32,255 acfm
Temperature F	212	175	80	80	80	70	70	70	500	700	500	200

TABLE 44. (Continued)

Major Compounds	56	57	58	59	60	61	62	63	64	65	66
Coal Solids											0.1
Sulfur	0.5										
Ash											15.9
Sodium											33.5
Calcium											
Water		100	100	100	100	100	100	100	100	0.5	84.0
Carbon Dioxide	99.5									7.6	
Nitrogen										89.8	
Oxygen										2.1	
Total Flow	35,255 acfm	8000 gpm	8000 gpm	55 gpm	55 gpm	25,000 gpm	25,000 gpm	412,000 lb/hr	121,520 lb/hr	141,155 acfm	3197 gpm
Temperature, F	80	60	90	60	100	60	90	310	212	300	145

packings, 28 ft^2/ft^3 for 2-inch Raschig rings. From the volume, a reasonable height and diameter were calculated.

The carbon dioxide absorber and desorber on the kiln gas stream were not designed in this exercise. The design parameters were estimated using a similar Union Carbide system estimate from 1978. This system was scaled up by using a 0.8 scale factor exponent on capital equipment and a 1.0 scale factor on materials and energy requirements.

Energy Balance. The energy needs for the hydrothermal and regeneration processes are summarized in Tables 45 and 46. For the Hydrothermal Section, the major energy need is that required to pressurize and heat the liquid. The only other uses are minor and include those for mixers and operating pumps for transporting the solutions through the system.

In the solid/liquid separation module, the primary energy need is for the evaporator, which is a direct coal-fired system with a steam economizer. Additional energy is required to operate the filter system for liquid withdrawal.

In the regeneration system, the major energy users are the kiln, which uses raw coal, and the steam stripper, which uses steam to remove CO_2 from the carbon dioxide stream. The large electricity consumers are the CO_2 compressor and the kiln gas compressor.

The major use of cooling water is in the regeneration module. The monoethanolamine tower requires most of this cooling water, but the cooling exchanger prior to precarbonation also represents significant major use.

In all calculations, steam is figured on the basis of coal by using 1.92×10^7 Btu/ton coal or an 80 percent efficiency of generation. This calculation assumes that all coal is the same as the coal feed and contains 2.4×10^7 Btu/ton.

The total energy (in tons of coal per hour) for the total system will require 50 tons of the 400 tons of treated coal production or about 13 percent of all production to sustain operations. In addition, 25.5 tons of raw coal are required to fuel the kiln. This brings the total coal usage to 75.5 tons per hour for hydrothermal processing.

TABLE 45. WESTLAND COAL CASE HYDROTHERMAL MODULE ENERGY

Using Unit	Steam Used, 10^6 Btu/hr	Electricity Used, kwh	Equivalent Coal, tons/hr
Caustic Storage	1.4		0.07
Fired Heater			12.45
Pressurization Pumps		4300	
Mixing and Pumping		930	
Totals	1.4	5230	12.52

TABLE 46. WESTLAND COAL CASE REGENERATION MODULE ENERGY

Using Unit	Steam, 10^6 Btu/hr	Electricity, kwh	Cooling Water, gpm	Equivalent Coal,(a) tons/hr
Precarbonation Cooler			8000	
Kiln System		50		25.5(b)
CO_2 Purification	391.4	16	25,000	20.4
Kiln Gas Compressor		2450		
CO_2 Compressor		2000		
Ash Centrifuge		200		
Lime Centrifuge		200		
CO_2 Cooler			460	
Mixers and Transportation		612		
Totals	391.4	5526	33,460	20.4 Treated 25.5 Raw

(a) For steam only.
(b) Raw coal.

Cooling water requirements for the system will amount to 33,500 gallons/minute. These requirements will be handled on-site by using a cooling tower.

Equipment Lists and Costs. In order to develop costs for the hydrothermal system, rough sizes had to be developed for equipment. Due to the wide variation in flow rate, inventory procedures were varied on a case-by-case basis. In all cases, inventory was maintained at no less than 6 hours when a major process is tied through a single unit to a preceding process. As an example, the coal inventory is maintained for 6 hours average because the mining and preparation systems are tied into the process through this module.

The only spare equipment included in the cost is that for the high pressure feed pumps and the pressure reduction system. Mixers are sized to provide Reynolds numbers in the 10,000 range, and are included in the total mix tank cost.

Heat exchanger design required estimation of heat transfer coefficients. For condensing Dowtherm A in the hydrothermal section, a coefficient of 125 Btu/hr-ft^2 was assumed. For the noncondensing Dowtherm A, a coefficient of 110 Btu/hr-ft^2 -F was assumed. For all other liquid heat exchangers, 120 Btu/hr-ft^2 -F was assumed as an overall heat transfer coefficient.

Towers were designed as plate towers except for the precarbonation tower, which is packed. In the tray towers, the Murphree efficiency was assumed to be 0.5.

The kiln system, CO_2 purification system, and sulfur plant are treated as miniature plants, and costs are quoted as battery limits structures. Tables 47 through 50 itemize equipment for the hydrothermal, solid/liquid separation, regeneration, and offsite modules, respectively. These equipment lists (keyed to Figures 28, 29, and 30) specify all major process items included in each section, with the exception of the kiln and CO_2 purification system, which are simply listed as modules.

Actual quotes were obtained to price the high temperature heat exchangers, the autoclave reactor, the kiln system, and the CO_2 purification system and sulfur plant. The rest of the plant was priced using costs scaled

Unit Identifier[a]	Unit Use	Unit Description	Bare Module Cost, $
H-1	Coal Feed Hopper	Silo hopper, 100,000 ft^3	$ 67.0
H-2	Caustic Feed Tank	20 ft dia x 25 ft height, CS tank with 25 HP mixer and internal heating coils	271.0
H-3	Lime Feed Storage	Lime hopper, silo style, 120,000 ft^3	97.0
H-4	Regenerated Leachant Feed Storage	250,000 gallon tank with 50 HP mixer	160.4
SL-1	Lime Slakers	Slaker train capable of 30 TPH slaking	296.0
C-1	Coal Conveyor	100 ft, 45 degree belt conveyor, 36 in wide	100.0
C-2	Lime Conveyor	150 foot, 30 degree belt conveyor, 14 in wide	65.0
P-1	Caustic Pump	20 gpm, 50 psig, low-carbon steel centrifugal pump	2.2
MT-1	Mix Tank	50,000 gal, low alloy covered tank	54.0
A	Autoclave	10,000 gallon nickel 201 high pressure, high temperature autoclave	10,638.0
FH	Fired Heater Loop Heat Exchangers	2-45,000 ft^3, CS shell/NI tubes, high pressure tubes, double pipe	12,088.0
	Fired Heater	240 million Btu/hr, low pressure Dowtherm	2,436.0
	Dowtherm Pump	Turbine pump, 4200 gpm at 40 psig, CS	53.0
P-2	Leachant Feed Pump	8,000 gpm, 40 psig carbon steel centrifugal pump	40.0
P-3	Mix Tank Recirculation Pump	10,000 gpm, 40 psig carbon steel centrifugal pump	55.5
P-5	Slurry Tank Recirculation Pump	10,000 gpm, 40 psig carbon steel centrifugal pump	55.5
P-4	High Pressure Feed Pumps	8-600 gpm, 1100 psig, carbon steel reciprocating pump	1,375.0
PR-1	Pressure Reduction Valves	2-CV 100, high pressure, hand regulated valves	50.0
W-1	Coal Weigh Station	400 ton/hr platform scale	29.4
W-2	Lime Weigh Station	50 ton/hr platform scale	29.5
MT-2	Coal Slurrving Tank	175,000 gallon carbon steel tank with mixing pump	115.0
MR-3	Pressure Letdown Tank	25,000 gallon vented process tank, carbon steel	25.0
	Total Equipment Costs		$28,100.0
	18 Percent Fee and Contingency		5,000.0
	Total		$33,100.0

(a) See Figure 28.

TABLE 48. WESTLAND COAL CASE SOLID/LIQUID SEPARATION SECTION EQUIPMENT LIST AND COSTS

Identifier[a]	Unit Use	Unit Description	Bare Module Cost, thousands
W-1	Washer	Rotary vacuum disk filter 3300 ft^2/filter with 30 HP centrifugal filtrate pump, 90,000 gallon tank, 40 HP agitator (8 units total)	$ 5,854
W-2	Washer		
W-3	Washer		
W-4	Washer		
W-5	Washer	Belt vacuum filter, 4400 ft^2/filter with 30 HP centrifugal filtrate pump, 90,000 gallon tank, and 40 HP agitator (8 units total)	3,996
W-6	Washer		
W-7	Washer		
W-8	Washer		
W-9	Washer		
W-10	Washer		
W-11	Washer		
W-12	Washer		
	Transfer Pumps	Centrifugal pump, 50 HP (13 units)	310
	Wash Water System	1.7 million gallon tank and 40 HP pump	408
	Surge Tank	0.8 million gallon tank	388
CE-3	Centrifuge Washer	Screen bowl centrifuge, 50 ton/hr solids, 285 HP with 90,000 gallon tank and 40 HP agitator (8 units total)	3,378
EV-1	Evaporation System	6-effect, backward feed, LVT evaporator, 40,000 feet of heat transfer service, 430 ton/hr evaporation rate, with 30 HP liquor transfer pumps	5,387
Total equipment costs			$19,721
18 percent fee and contingency			3,550
Total			$23,271

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[a] See Figure 29.

TABLE 49. WESTLAND COAL CASE REGENERATION SECTION EQUIPMENT LIST AND COSTS

Unit Description(a)	Unit Use	Unit Description	Bare Module Cost, thousands
EX-1	Heat Exchanger	6,000 ft^2 carbon-steel shell and tube exchanger	$ 147
EX-2	Heat Exchanger	27,000 ft^2 carbon-steel shell and tube exchanger	370
T-1	Precarbonation Tower	2-43 ft tall by 14 inch carbon steel spray towers packed with 1/2 inch Raschie Rings	66
T-2	Carbonization Tower	2-50 ft tall by 14 inch carbon steel towers with valve trays	158
T-3	Decarbonization Tower	1-20 ft tall by 60 inch diameter carbon steel tower with 10 valve trays	76
MT-4	Liming Tank	70,000 gallon tank with 15 HP mixer	53
CE-1	Ash Centrifuge	50 ton/hr solids screen bowl centrifuge with 200 HP motor	66
CE-2	Lime Centrifuge	50 ton/hr solids screen bowl centrifuge with 200 HP motor	66
FH-2	Lime Kiln and Dryer	60 ton/hr kiln with dew point scrubber and 2 solid feed systems	6,629
T4 & T5	CO_2 Purification	2-14 inch by 50 ft MEA towers with associated exchangers, pumps and scrubbers	8,967
CO-1	Kiln Gas Compressor	3285 BHP compressor without coolers	2,155
CO-2	Carbon Dioxide Compressor	1900 BHP compressor with coolers	1,141
H-5	Carbon Dioxide Reservoir	240,000 ft^3 horizontal gas storage at 15 psig (8 units)	2,600
EX-3	Steam Stripper Exchanger	30,000 ft^2 carbon steel shell and tube exchanger	620
P-6 P-11	Pumps for Towers T-1 to T-3	65 HP centrifugal pump, carbon steel (6 pumps)	120
P-12	Regenerated Leachant Pump	170 HP centrifugal pump, carbon steel	40
EX-4	Carbon Dioxide Cooler	1500 ft^2 carbon-steel shell and tube exchanger, 50 psig rating	58
OC-1 & 2	Condensate Collectors	1000 gallon liquid/gas separators (2)	31
H-6	Lime Storage and Handling	12,000 ft^3 hopper with conveyor	183
	Total Equipment Costs		$23,346
	Contingency and Fee		4,806
	Total		$28,152

(a) See Figure 30.

In comparing these costs, it is apparent that all three estimates are reasonably close, the capital variance being less than 11 percent and the operating cost variance being approximately 20 percent. Considering various uncertainties contained in any estimation method, such variances are within the expected range of accuracy.

Process Uncertainties. Of even more concern are the uncertainties involved with the Process Modifications. The heat exchangers and reactor in the hydrothermal process have been sized and estimated assuming use of nickel alloy. Data for materials estimates in the 1975 Summary Report(5) indicated that carbon steel could be used instead. Similar equipment for paper treatment processes is made of carbon steel. Should such a change be possible, a savings of approximately 25 percent is projected for the hydrothermal section capital cost, which is $1.17 per ton operating cost.

Another savings, potentially larger, is to use raw flue gas or the CO_2 from the tail gas of the sulfur plant to do the precarbonation. This could save 30 percent of the MEA plant operating and capital cost, which is approximately another $1.50 per ton of operating cost. These savings are not incorporated into the estimate in Table 51, primarily because they are high risk and yet comprise only a small percentage of cost avoidance.

Cost Effects of Sulfur Removal. Sulfur removal requirements can have an impact on economics, depending on how the process is modified to treat the coal to enhance or reduce the sulfur removal from the coal.

Not much can be done to increase the sulfur removal, since currently almost all the pyritic sulfur and about 30 percent of the organic sulfur are being recovered in the hydrothermal process. Since removal in many cases exceeds that required to meet some emission standards, less sulfur could be removed in the process.

There are two potential mechanisms for reducing sulfur removal: reducing the feed sodium or recycling the unregenerated leachant. Each mechanism is dependent on the amount of free sodium available to capture sulfur in the reaction.

In the 1975 Battelle Summary Report(5) on hydrothermal treatment, Chauhan and others reported that the reaction rate, r_a, between sulfur and the available sodium is a reaction of the form,

$$r_a = kC_aC_b^2$$

where C_a represents the concentration of sulfur able to be removed ultimately, and C_b is the concentration of sodium available to react with the sulfur.

The equation governing the reaction in a continuously mixed flow through autoclave can be developed from the material balance and the reaction rate. The equation becomes:

$$\frac{V}{F} = \frac{C_i - C_a}{kC_aC_b^2} \quad ,$$

where C_a = Outlet sulfur concentration, lb/ft^3

C_b = Outlet free sodium concentration, lb/ft^3

C_i = Inlet sulfur concentration, lb/ft^3

F = Flow rate through the reactor, ft^3/minute

k = Kinetic constant of reaction, minute - ft^6/lb^2

V = Reactor volume, ft^3 .

Rearranging this equation yields:

$$C_a = \frac{C_i}{(1 + kC_b \frac{2V}{F})} \quad .$$

This equation indicates that reduction in the free sodium is probably the most effective variable to manipulate. In fact, since the value of the second term is equal to the sulfur removed divided by the sulfur left, this term is much larger than 1. A change in removal, then, from 95 percent to 80 percent of the removal sulfur is accomplished by reducing the available sodium 10 percent. This can be done by reducing the feed sodium by about 10 percent, or by recycling 30 percent of the unregenerated leachant. The latter course is considered more cost effective because a more significant capital and operating cost reduction can be produced by recycle. To calculate the benefit, the capital cost is assumed to be a function of (1.0 - recycle fraction)$^{0.6}$. Thus, for a \$33-million regeneration system investment and a \$10-million offsite boiler investment, a system with recycle of 30 percent of the total leachant will cost 20 percent less in capital charges and 30 percent less in raw and treated coal costs in the regeneration section (about $1.20 less). In a total cost of $35, about 6 percent can be saved by reducing the recovered sulfur.

However, if the washing requirement to remove sodium could be eliminated, the costs could be reduced by about $6.00 per ton, which would be worthwhile. Potentially, using either less sodium, or possibly potassium in lieu of sodium offers a larger savings than recycle of untreated leachant alone.

Process Alternatives. One alternative which appears promising is to use ferrous carbonate to remove the sulfur from the leachant. The ferrous carbonate system, shown in Figure 31, replaces the regeneration system in Figure 30. In this case, a sulfuric acid plant would replace the sulfur plant used for conversion of the hydrogen sulfide. The process material balance is presented in Table 53. The table lists additive, product, and intermediate streams assuming a 30 percent moisture cake consistency in each centrifuge and 5 to 10 percent excess reagent in each additional stream. The ferrous carbonate addition is assumed as 1.5 times stoichiometric.

The equipment list for the regeneration section is presented in Table 54. The equipment consists of centrifuges and mixing tanks. The mixing tanks are sized at approximately 15 minute retention. Centrifuges are sized assuming solids similar to coal.

No equipment list was prepared for the offsite section. The main modification to Table 54 is an increase in cooling tower size to handle the increased cooling necessitated by running low temperature reactions in all vessels. The lime storage is roughly doubled and sodium carbonate and ferrous sulfate storage are added. The cost of adding this storage and cooling offsets the steam boiler in Table 50.

The economics of this process are presented in Table 55. The costs for the separation and hydrothermal sections remain the same. The sulfuric acid plant costs are obtained from a quote by Monsanto Envirochem using a standard sulfuric acid plant.

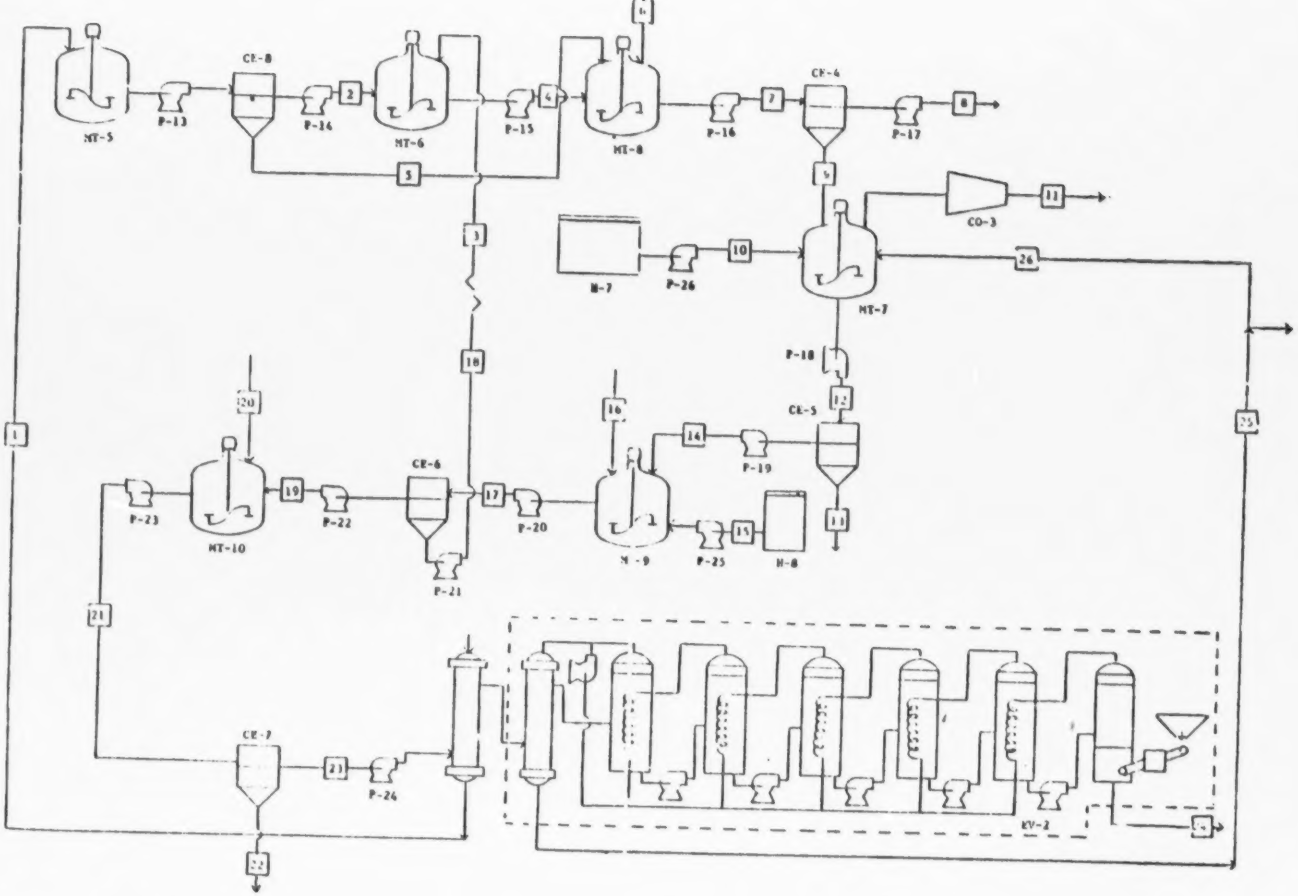
MT-5
P-13
CE-8
P-14
2
MT-6
P-15
4
6
MT-8
P-16
7
CE-4
P-17
8
5
9
3
CO-3
11
M-7
P-26
10
26
MT-7
P-18
12
CE-5
18
20
16
14
P-19
1
25
P-23
MT-10
19
P-22
CE-6
17
P-20
M-9
P-25
15
M-8
13
P-21
21
CE-7
23
P-24
EV-2
24
22

FIGURE 31. FERROUS CARBONATE REGENERATION PROCESS FOR WESTLAND COAL SPENT LEACHANT (See Table 54) for Identifiers)

TABLE 53. WESTLAND COAL CASE $FeCO_3$ REGENERATION

	Stream (See Figure 31)												
	1	2	3	4	5	6	7	8	9	10(b)	11	12(c)	13
Cations, %[(a)]													
H^+										2.1		0.01	
Na^+	3.5	3.7	22.5	4.6			4.3	4.8					
Ca	1.6		0.5		36.0	19.0	1.8	0.1	17.5			2.6	15.7
Fe			27.3	1.3			1.2		12.4			1.9	0.6
Anions, %													
OH^-	3.9	2.2		2.1	30.6	15.0	3.4	3.5	2.5				
S^-	0.5	0.5		0.5			0.5		4.7				
$CO_3^=$			29.3	1.4			1.3		13.3				
$SO_4^=$			1.0	0.05			0.003	0.05	0.4	97.9		10.1	38.6
Neutral, %													
Coal Solids	0.3	0.4		0.3			0.3	3.2				0.5	2.9
H_2S											34.0		
CO_2											66.0		
Other Solids	1.7	1.8		1.7								2.4	14.6
H_2O	89.0	91.5	19.5	88.1	33.4	66	85.5	91.6	30.0			82.6	27.6
Total Flow	3231 gpm	3178 gpm	44.1 t/hr	3212 gpm	39.3 t/hr	17.3 t/hr	3312 gpm	3197 gpm	96.1 gpm	102 gpm	4595 scfm	2140 gpm	105.1 t/hr
Temperature, F	190	80	75	70	70	70	70	70	70	70	70	70	70

(a) Units in percent except where noted.

(b) H_2O increased by $CO_3^=$ and OH^- conversion.

(c) S.G. H_2SO_4 (100%)=1.8255.

TABLE 54. WESTLAND COAL CASE; $FeCO_3$ EQUIPMENT LIST AND COSTS

Identifier[(a)]	Unit Use	Unit Description	Bare Module Cost, thousands
MT-5	Mixing Tank		
MT-6	Mixing Tank	30,000 gallon mixing tanks, carbon steel; includes	$ 713.0
MT-7	Mixing Tank		
MT-8	Mixing Tank	6-50 HP mixers, carbon steel	129.0
MT-9	Mixing Tank		
MT-10	Mixing Tank		
H-7	H_2SO_4 Storage Tank	1.5 mm gal., stainless steel	3,076.0
H-8	Na_2CO_3 Storage Tank	65,000 ft , carbon steel	455.0
H-9	Lime Storage Tank	125,000 ft , carbon steel	763.9
CE-4	$Ca(OH)_2$ Centrifuge	80 HP; includes 250 HP motors	2,812.5
CE-5	$CaSO_4$, $CaCO_3$, FeS, $Fe(OH_2)$ Centrifuge		
CE-6	$CaSO_4$ Centrifuge		
CE-7	$FeCO_3$ Centrifuge		
CE-8	$CaSO_4$ Centrifuge		
P-13 to P-17	Transfer Pumps	4000 gpm at 20 psig, carbon steel	62.2
P-18 to P-25		3000 gpm at 20 psig, carbon steel	50.5
P-26		150 gpm at 20 psig, inconel	58.0
CO-3	H_2S, CO_2 Compressor	300 HP Compressor	204.2
SL-2	Lime Slaker	Slaker train, 535 tons/day	296.0
WC-1			
WC-2	Weigh Conveyor	1000 tons/day	378.0
WC-3			
EV-2	Evaporation System	6 effect, backward feed, nickel	12,371.0
			$21,368.0
	Contingency and Fee		3,846.3
	Total		$25,214.3

(a) See Figure 31.

TABLE 55. WESTLAND COAL CASE COSTS FOR HTT TREATMENT USING FERROUS CARBONATE FOR REGENERATION

	Hydrothermal Section	Solid/Liquid Separation	Regeneration	Sulfuric Acid Production	Offsite Requirements	Total
Fixed Capital, $\$10^6$	39.7	23.3	25.2	11.8	46.9	$146.9
Working Capital, $106					18.0	18.0
Cost Contributions, $/ton						
Raw Materials						
Na_2CO_3			3.70			3.70
NaOH		0.75				0.75
Lime	1.49		1.18			2.67
H_2SO_4			5.78			5.78
$FeSO_4$			0.31			0.31
Miscellaneous		0.32				0.32
Coal						
Treated	1.43	1.41	2.21			5.05
Raw						
Utilities	0.44	0.70	0.39	0.05	0.15	1.73
Labor Related	0.18	0.36	0.36	0.10	0.16	1.16
Capital Related	2.42	1.42	1.44	0.72	3.96	10.06
Penalties (Credits)		4.12	(6.43)(a)	(1.75)(b)	-	(4.06)
Total Operating Cost	5.96	9.08	9.04	-0.88	4.27	27.47
Profit, Taxes, and Interest	2.29	1.35	1.46	0.75	3.74	9.59
Total Processing Cost, $/ton	8.25	10.43	10.50	-0.13	8.01	$ 37.06

(a) Caustic credit minus landfill costs

(b) Credit for H_2SO_4 used in regeneration.

The offsite working capital in Table 55 varies from that in Table 51 due to the need for an inventory of sulfuric acid, sodium carbonate, and ferrous sulfate, and an increase in the lime inventory.

When the economics of this case are compared with CO_2 regeneration, the costs appear about the same. The use of mixer settler tanks in lier of centrifuges could reduce the $FeCO_3$ capital cost markedly. Similarly, reduction of the ferrous carbonate addition can save both sulfuric acid and sodium carbonate costs, reducing both regeneration and offsite costs. Optimization of these factors and some more experiments are recommended.

Colstrip Coal

The Colstrip coal case is considered to be typical of Western subbituminous coal treatment. The process characteristics are such that 135 gallons/minute of brine are thrown away. The brine contains a fairly high proportion of dissolved sodium, magnesium, and calcium salts and other ash constituents. The process uses only water and dispersant for raw chemicals to treat the coal rather than a true mixed leachant.

The coal composition, before and after treatment, is listed in Table 56. The removal of sodium and sulfur from the coal is sufficient to qualify the treated coal as a boiler fuel. The moisture content is not affected much by the treatment. The moisture is increased by approximately 1 percent and thus only derates the coal for combustion purposes by about 2 percent.

TABLE 56. COLSTRIP COAL TREATMENT SUMMARY

Raw Coal, percent		Treated Coal, percent
Coal Solids (MAF)[a]	99.06	99.28
Sulfur (MAF)(a)	0.94	0.27
Ash (MF)(b)	9.78	9.15
Na(MF)(c)	0.02	0.01(d)
Ca(MF)(c)	1.14	1.04
Mg(MF)(c)	0.43	0.38
Water	19.01	20.03

(a) MAF: Moisture and ash free basis.
(b) MF: Moisture free basis.
(c) Contained in ash.
(d) Lower limit of material balance accuracy; actual value is about 0.008 percent moisture-free.

Process Description. The process used for treatment of Colstrip coal is shown in Figure 32. The process used for hydrothermal treatment is modified compared to the Westland case. First, no chemicals are added. Second, this hydrothermal processing uses water and chemicals recovered from the coal to treat the coal. And, third, residual sulfur and ash are recycled in the liquid stream to conserve water.

The coal is heated by direct exchange with the reactor effluent. The additional heat for maintenance of the reaction temperature is supplied by a fired heater using Dowtherm A as a circulating medium. All heat exchangers are fabricated from carbon steel because the sodium content is low enought to minimize stress corrosion cracking.

The reactor, similarly, is constructed of carbon steel and has a 10,000 gallon volume with a rating of 1500 psig pressure at 550 F. The reactor effluent is cooled by the reactor influent in a countercurrent heat exchanger. The pressure reduction of the effluent is accomplished through a valve as in the Westland case.

The solid/liquid separation section has no washing. The coal is dewatered by a centrifuge and conveyed to storage.

Of the leachant coming out of the coal, 70 percent is returned to the leachant storage tank for direct recycle. The remaining 30 percent is passed through a clarifier where settling and oxidation are allowed to take place. Then a three-stage reverse osmosis unit is used to remove roughly 90 percent of the water. The remaining 10 percent is passed to a clay-lined pond for storage, as well as natural evaporation; this treatment step is the same as that employed in handling desulfurization wastes.

Material Balance. The material balance for each stream of the process is given in Table 57. This balance was prepared from experimental data obtained on water and coal treatment at a 3:1 ratio and extrapolated to a 2:1 ratio. The change in concentration for soluble substances in the coal varies from the 3:1 case since the water carried with the product coal is assumed to have the same concentration of soluble species as does the leachant separated from the coal. For instance, treatment with a 4:1 water/coal ratio should leave less sulfur in the coal than a 3:1 water/coal treat-

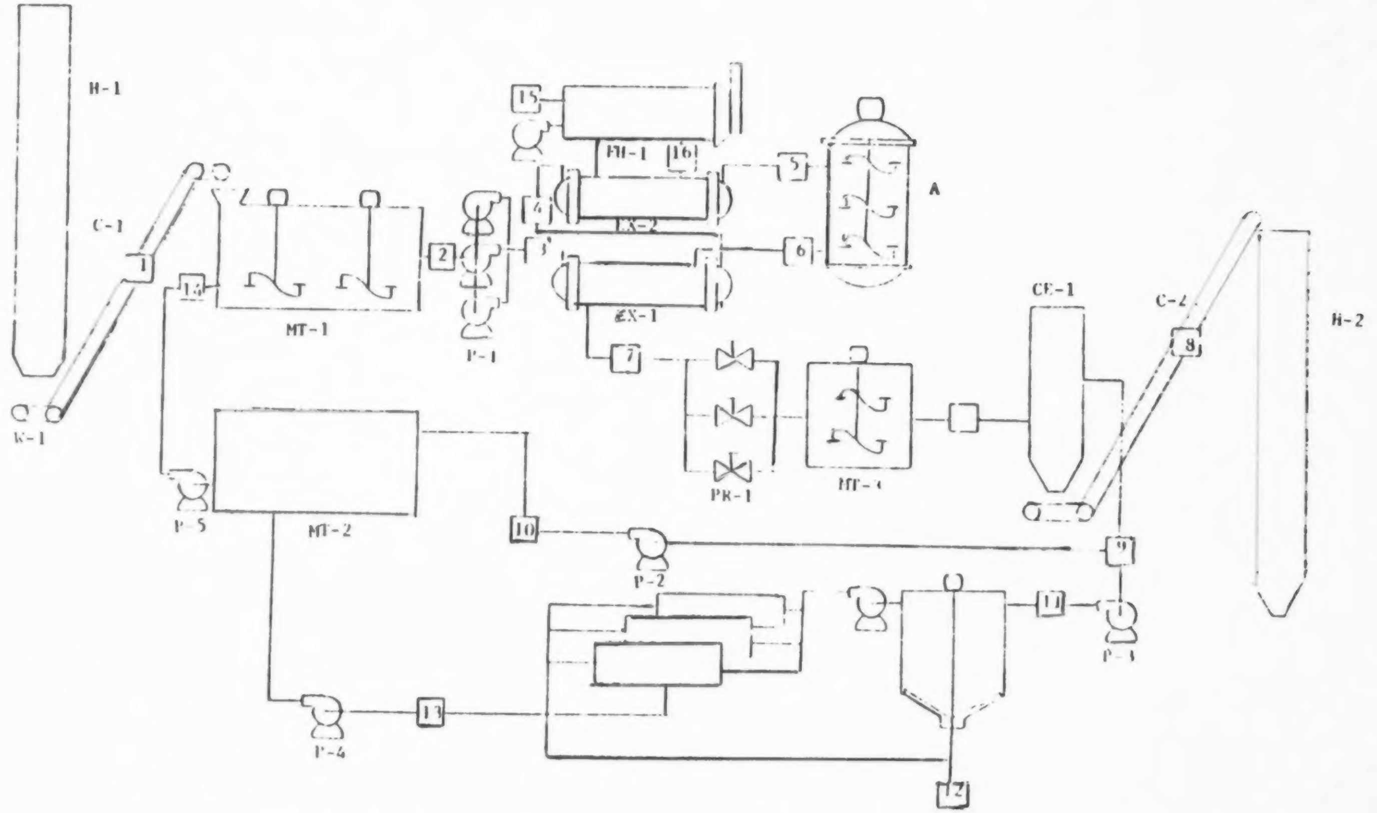
H-1
C-1
R-1
1
14
MT-1
2
P-1
3
4
15
FH-1
16
EX-2
5
6
A
EX-1
7
PR-1
CE-1
C-2
8
H-2
MT-2
P-5
10
P-2
9
11
P-3
P-4
13
12

FIGURE 32. HYDROTHERMAL TREATMENT PROCESS FOR COLSTRIP COAL
(See Tables 58-60 for Identifiers)

TABLE 58. COLSTRIP COAL CASE HYDROTHERMAL TREATMENT EQUIPMENT COSTS

Unit Designation(a)	Unit Description	Unit Specifications	Cost, $ thousands
H-1	Coal Storage Hopper	100,000 ft^3 silo-type storage hopper	$ 67
C-1	Coal Conveyor	36 inch, 100 ft, belt conveyor	100
W-1	Coal Weigh Station	400 t/hr feed station	68
MT-1	Coal Slurrying Tank	250,000 gallon carbon steel tank with mixers	160.4
P-1	High Pressure Pumps	8-1100 psig at 600 gpm multicylinder pumps	9,247
EX-1	Autoclave Exchanger	25-10,000 sq ft heat exchangers, CS, high pressure	5,747
EX-2	Dowtherm Condenser	12,000 sq ft heat exchanger, CS, h-p tubes	250
A	Autoclave	50,000 gallon stirred reactor, 1500 psi, CS	3,347
FH-1	Fired Heater	110 million Btu delivery, 40 psig drum heater	888.7
PR-1	Pressure Reduction	2 high pressure, Cv 100 valves	50
			$19,925.1
		Contingency and fee at 18 percent	3,565.9
		Total	$23,491.0

(a) See Figure 32.

TABLE 59. COLSTRIP COAL CASE SOLID/LIQUID SEPARATION SEPARATION SECTION EQUIPMENT COSTS

Unit Disignation[a]	Unit Description	Unit Specifications	Cost $ thousands
CE-1	Centrifuges	8-50 ton/hr screen bowl centrifuges	$ 5,500
C-2	Product Coal Conveyor	36 inch, 100 ft, belt conveyor	100
H-2	Product Coal Hopper	100,000 ft^3 silo type storage hopper	67
MT-3	Centrifuge Feed Tank	250,000 gallon carbon steel tank mixers	160.4
			$ 5,827.4
		Contingency and Fee at 18 Percent	$ 1,047.5
		Total	$ 6,874.9

(a) See Figure 32.

TABLE 60. COLSTRIP COAL CASE REGENERATION SECTION EQUIPMENT COSTS

Unit Designation[(a)]	Unit Description	Unit Specifications	Costs, $ thousands
MT-2	Leachant Storage Tank	1,900,000 gallon carbon steel tank	$ 445.7
MT-4	RO Feed Tank	250,000 gallon carbon steel tank $\bar{c}$ mixers	160.4
RO-1	Recycle Osmosis Unit	3 stage unit at 1.4 mm gal/day inlet, 1000 psig	2,800
P-2	Recycle Pump	3000 gpm at 50 psig CS pump	40
P-3	Water Feed Pump	3000 gpm at 50 psig, CS pump	40
P-4	Waste Pump	250 gpm at 50 psig, CS pump	5.5
P-5	Leachant Feed Pump	3000 gpm at 50 psig, CS pump	40
			$ 3,531.6
		Contingency and Fee at 18 Percent	371.1
		Total	$ 3,902.7

(a) See Figure 32.

TABLE 61. COLSTRIP COAL CASE OFFSITE EQUIPMENT

Equipment Description	Cost $ thousands
Coal storage at 60 lb/ft^3, $143/t, 15 days (4,800,000 ft^3)	$20,592
Sludge disposal pond, 180 mm gal for 12 yr operation	2,391.7
Sodium lauryl sulfate storage	112.0
	$23,095.7
Incidentals (11 percent)	2,529.5
	$25,625.2
Contingency and Fee at 18 Percent	4,594.5
Total	$30,219.7

TABLE 62. COLSTRIP COAL CASE ECONOMIC SUMMARY

	Hydrothermal Treatment	Solid/Liquid Separation	Regeneration	Offsite and Ash Disposal	Total
Fixed Capital, $ millions	23.5	6.9	3.5	30.2	63.7
Working Capital, $ millions				3.1(a)	3.1(a)
Contribution to Price, $/ton					
Dispersant		0.65			0.65
Treated Coal	0.23				0.23
Flocculant			0.04		0.04
Utilities	0.41	0.12	0.19	0.10	0.82
Direct Labor	0.12	0.12	0.08	0.16	0.48
Capital Related	1.43	0.42	0.26(b)	2.02	4.13
Total Operating Costs	2.19	1.31	0.57	2.28	6.35
Profit, Taxes & Interest	1.36	0.39	0.20	1.92	3.87
Total Treatment Cost	3.55	1.70	0.77	4.20	10.22

(a) Working capital is arbitrarily assessed to offsites.

(b) Maintenance cost for reverse osmosis unit calculated at $.06/ton excess over standard percentage assumption.

Basis: 3,456 million tons/year into process.

ton. The estimated total value of a ton of clean coal is $18.97 including purchase price. Transportation costs must be added to this cost.

Process Alternatives. Some consideration has been given to using an evaporator after the reverse osmosis unit to recover water which is now thrown away. The capital cost for such a unit would be about $600,000 if recovery of all but about 20 gpm was achievable (98 percent recovery). This evaporator would raise the reject stream to 80 percent solids. The energy requirements for a 6-effect, backward-feed evaporator for such water recovery would add an energy requirement of 2 tons of coal per hour at a cost of 5 cents per ton of coal processes. The capital cost is about 8 cents a ton, so 17 gallons of water per ton of coal could be recovered. The process water cost is about $7.65/1000 gallons of water, which is considered to be well above the raw water costs even for the Western badlands area.

Homer City Coal (Physical/Hydrothermal Treatment)

Homer City coal is mined in western Pennsylvania, near Pittsburgh. This coal is a high-sulfur, high-ash coal. The coal is currently cleaned by an advanced physical beneficiation process to produce three fractions. The deep clean fraction which constitutes about 25 percent of the raw coal feed contains about 0.88 percent sulfur. This fuel, which meets New Source Performance Standards as a clean fuel, is burned in a new boiler complex. A second fraction, which constitutes about 50 percent of the raw coal, contains 2.2 percent sulfur. This fuel is currently burned in older boilers which are not regulated by the New Source Performance Standards. The third fraction which constitutes about 25 percent of the raw coal is refuse.

If hydrothermal treatment were used on the high-sulfur fraction, and this blended with the deep cleaned fraction, quantity of fuel which meets New Source Performance Standards, would be increased to about 75 percent. With this objective, fuel costs employing a combined physical/hydrothermal process were developed for a facility cleaning 800 tons/hr of Homer City coal. The assumptions were made that 50 percent (400 tons/hour) of the raw coal would be hydrothermally treated.

Process Description. The combined physical/hydrothermal process used for this case is shown in Figure 33. This process combines the existing physical cleaning process with a proposed hydrothermal process. The hydrothermal process proposed is essentially identical to that used for treating Westland coal.

Material and Energy Balances. The material and energy balances are presented in Tables 63 through 65 which are correlated to Figures 28 to 30. The system design is the same as for Westland coal. The balances are very similar to those for the Westland coal, with slightly more sodium and calcium consumption. The increased calcium consumption is marked by the increase in ash (Stream 37, Figure 34) between the Westland and Homer City cases. The majority of the ash is limestone produced from calcium precipitation. Thus, the ash (except for a small blend stream) could be added to Stream 51 (Figure 34) to be reconverted to lime and carbon dioxide.

The energy requirements are very similar to those for the Westland coal case. The total coal required is still 33 tons of treated coal and 25 tons/hour of raw coal for processing.

Process Economics. The process economics for physical treatment are presented in Table 66. These costs are based on capital and operating costs from Reference 8, which are then updated to 1978 dollars. No distinction could be made between processing costs for the deep cleaned and middle fraction coal coming out of the process, so the costs were summarized identically. Assumptions made for the required revenue in the economics evaluation of physically cleaned coal were the same as those for all the hydrothermal processes, since the intangible costs of depreciation, taxes, interest, and other factors could not be obtained from a documentable source.

The hydrothermal process economics are summarized in Table 67. These costs are developed from the capital requirements and equipment lists for Westland coal processing, since the equipment is virtually identical. The operating raw materials reflect the increases of sodium and calcium required for the system. The increased waste disposal needs are contained in the penalty section of the regeneration system.

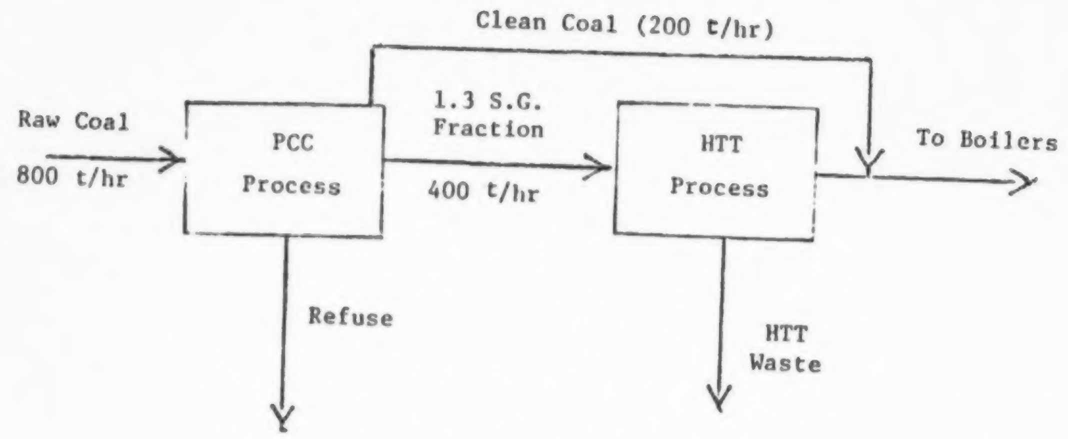
Clean Coal (200 t/hr)
Raw Coal
800 t/hr
PCC
Process
1.3 S.G.
Fraction
400 t/hr
HTT
Process
To Boilers
Refuse
HTT
Waste

FIGURE 33. RELATIONSHIP BETWEEN THE PHYSICAL COAL CLEANING (PCC) PROCESS AND THE HYDROTHERMAL TREATMENT (HTT) PROCESS FOR HOMER CITY COAL

TABLE 63. PHYSICAL/CHEMICAL COAL CLEANING CASE - HYDROTHERMAL SECTION MATERIAL AND ENERGY BALANCE

Major* Compounds	See Figure 28											
	1	2	3	4	5	6	7	8	9	10	11	12
Coal Solids, %			72.5				25.0	21.4	21.4			
Sulfur, %			2.3				0.8	0.7	0.7			
Ash, %	50	100	20.2	10.7	35.9	10.7	14.0	17.5	17.5			
Na	28.5		0.02	6.2	4.4	6.2	4.1	4.4	4.4			
Ca		71.4	0.07		15.3		0.02	2.1	2.1			
H_2O, %	50		5.0	89.3	64.1	89.3	60.3	60.4	60.4			
Dowtherm A, %										100	100	100
Total Flow	31.6 gpm	40 t/hr	400 t/hr	480 gpm	480 gpm	2718 gpm	2798 gpm	3278 gpm	3278 gpm	4153 gpm	4153 gpm	4153 gpm
Temperature, F	80	80	80	80	80	80	80	80	527	700	100	500

* Percent except where noted

TABLE 63. (Continued)

Major Compounds	See Figure 28					
	13	14	15	16	17	18
Coal Solids	21.4	21.4	22.9			43.9
Sulfur	0.7	0.7	0.7			0.3
Ash	17.5	17.5	18.6			11.8
Na	4.4	4.4	4.7			0.7
Ca	2.1	2.1	2.3			3.3
H_2O	60.4	60.4	58.0	100	100	42.0
Total Flow	3278 gpm	3278 gpm	3278 gpm	79.6 t/hr	19.2 t/hr	12.2 t/hr
Temperature, F	525	312	220	220	220	80

TABLE 66. COSTS FOR PHYSICAL CLEANING OF HOMER CITY COAL

	Middling[a]	Deep Clean[a]	Total[a]
Capital Cost, $ millions	$22.2	$9.8	$32.0
Working Capital, $ millions			2.0
Cost to Process, $/ton Product Coal			
Operations & Maintenance[a]	1.03	1.03	1.03[b]
Capital Charges[a]	0.99	0.99	0.99
Moisture Penalty (Drying)[a]	0.20	0.20	0.20
Total Operating Cost	2.22	2.22	2.22
Profit, Taxes & Interest	1.61	1.61	1.61
Total Operating Cost, $/ton	3.83	3.83	3.83

(a) Based on Reference 8.

(b) Based on similar assumptions in hydrothermal economics.

Basis: 4.37 million tons per year total coal produced; raw coal cost is $13/ton.

TABLE 67. COSTS FOR HYDROTHERMAL TREATMENT OF HOMER CITY COAL

	Hydrothermal	S/L Separation	Regeneration	Sulfur Plant	Offsites	Total
Capital Costs, $1,000	39.7	23.3	26.6	13.8	56.4	159.8
Working Capital, $1,000					14.6	14.6
Contributions to Cost, $/ton						
Raw Materials						
NaOH		0.75				0.75
Lime	2.80					2.80
Miscellaneous Chemicals		0.65	0.03	0.15		0.83
Coal						
Treated	0.71	1.01	0.93			
Raw			1.24			
Utilities	0.46	0.38	0.79	0.13	0.04	1.80
Labor Related	0.18	0.36	0.36	0.07	0.18	1.15
Capital Related	2.42	1.42	1.63	0.84	3.42	10.64
Penalties (Credit)		2.78	1.08	(0.62)		0.46
Total Operating Cost	6.57	7.35	6.06	0.57	3.64	24.19
Profit, Taxes, and Insurance	2.30	1.35	1.54	0.80	4.11	10.10
Total	8.87	8.70	7.60	1.37	7.75	34.29

Basis: 3.456 million tons/year; feed coal is $19.89/ton.

The combined physical/HTT treated coal will cost about $24.14, since 375 equivalent tons are processed at $34.29/ton, and 200 tons are processed at an estimated cost of $3.80/ton for physically cleaned coal. The raw coal used in the process is assumed to cost $31.00/ton based on the premise that it is raw hydrothermal feed coal. The processed coal used is assumed to cost $24.14, which is the estimated selling price for blended physical HTT cleaned coal.

One savings that could be realized in this case would result from the elimination of the middle fraction dryers in the physical cleaning process. The wet coal could be sent directly to the hydrothermal process. The process modification recommendations contained in the Westland coal case are still applicable to this case.

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APPENDIX 1

LIQUID-SOLID SEPARATION AND WASHING ALTERNATIVES

Liquid-Solid Separation Alternatives

A complete liquid/solid separation system consists of one or more of the following four steps:

1. Pretreatment
2. Solids concentration
3. Solid separation,
4. Posttreatment.

Pretreatment, either chemical (flocculation, dispersion, etc.) or physical (aging, filter aid additions, etc.) prepares the slurry for efficient separators. Solids concentration through gravity sedimentation provides a more concentrated slurry which results in a reduced volume requiring separation and usually an increased separation rate. Solids separation, by either pressure, vacuum, or gravity filters or centrifuges removes the solids from the slurry. Posttreatment includes washing (displacement or repulp) drying, and/or deliquoring by mechanical compression.(1)*

Primary emphasis of this study was on the solids separation and pretreatment steps. However, for the separation of the unbound sodium and water from the treated coal, techniques involving all four steps were investigated.

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* See Reference List on page 182.

Selection of Separation Equipment

A large variety of potentially applicable separation equipment is available. The selection process normally begins with an investigation of cake formation rate. Selection of separation equipment is dependent on rate of cake formation and filtration rate. Cake formation rates are typically described as rapid, medium, and slow filtering in the literature. Quantitative and subjective descriptions of the three levels are presented in Table 1-1.

TABLE 1-1. FILTRATION CHARACTERISTICS(2)

Filtration Range	Cake Formation Rate	Characteristics	Leaf Test Rate,* ton/hr/ft^2	Filtrate Rate, gal/min/ft^2
Rapid filtering	72 in./sec	High concentration, fast settling, hard to suspend	>.25	> 300
Medium filtering	0.02-2 in./min	Forms cake easily, can be suspended, medium solids content	0.025 to .25	12-300
Slow filtering	0.05-2 in./hr	Low solids concentration, high filtration resistance, tendency to blind media	0.006 to 0.025	0.6 to 12

* Separation data, obtained on HTT coal, showed that filtration rate is dependent on the degree of processing.

As noted in Table 1-2, the rate ranges from medium to rapid filtering. In order to take advantage of the increased filtration rates, different types of equipment were specified for the separation system. Using the information in Table 1-3, drum and disc filters were selected for this segment. These were selected since they are the least expensive of continuous vacuum filters and can be used with slurries containing 40 to 50 percent solids.

TABLE 1-2. FILTRATION DATA FOR HYDROTHERMALLY TREATED COAL(a)

Solids Treatment	Cake Formation Rate,	Leaf Test Rate, ton/hr/ft^2	Filtration Rate,
Raw HTT Clurry	in./hr	0.03	14.5
First Cake Washing	in./min	0.23	10.3
Second Cake Washing	in./min	0.33	147.
Third Cake Washing	in./sec	0.47	136.

(a) Results for minus 50 mesh-run coal treated in the batch autoclave and separated with the use of surfactants.

TABLE 1-3. APPLICABLE FILTRATION EQUIPMENT(a)

Filter Type Filter Type	Applicable Filtration Range			Normal Solids Range Applied
	Rapid Filtering	Medium Filtering	Slow Filtering	
Continuous Vacuum Filters				
Multicompartment drum	X	X	X	7-50
Singlecompartment drum	X			7-50
Scroll discharge	X	X		7-50
Tilting pan	X	X		10-50
Belt	X	X		10-50
Disc		X	X	5-50
Batch Pressure Filters				
Plate and frame		X	X	1-10
Vertical leaf		X	X	< 1
Tubular		X	X	< 1
Horizontal plate	X	X	X	< 1

(a) Reference 3.

In addition to filtration, separation by centrifuges was also studied. The advantage of lower cake moisture content was countered against the greater capital, labor, and utility costs for centrifuges in a comparison of the two basic separation alternatives.

WASHING ALTERNATIVES

The makeup cost of residual sodium left in the washed coal is the second highest cost component for the separation and washing section. Therefore, methods to more efficiently wash the sodium from the treated coal were explored. Efficiency of the washing methods was assessed in terms of

- Quantity of wash water
- Number of washing stages
- Type of separation equipment.

The quantity of washwater plays an important economic role because the greater the quantity of washwater used, the greater the quantity of sodium removed for recovery; however, excess water must be evaporated prior to regeneration or recycle of the leachant.

The number of stages is important because the capital cost component is directly proportional to the number of separation and washing stages.

The type of separation equipment applicable for a particular type of washing also is important because costs, in terms of $/sq ft of separation area, vary greatly depending on the type of equipment.

The type of washing operation also plays an important role because it influences all three factors. The two basic types of washing methods available, displacement and repulp washing, have advantages and disadvantages.

Displacement Washing

In displacement washing, the wash liquor pushes the filtrate ahead of it through the void channels with practically no filtrate dilution. With a well-formed, permeable cake, the bulk of the original liquor held in the cake voids can be readily replaced by wash liquor. The action of displacement washing works best with thin cakes, but can be employed with thicker cakes when they are noncompressible. Normally, the filtrate is displaced without dilution by the first volume of washing giving about 90 percent filtrate removal. Two additional volumes can normally displace about 50 percent each of the original liquor still remaining in the cake. Removal of the remaining soluble materials takes much longer because the original liquor is held by individual particles and must be replaced by diffusion(4). For example, an HTT coal cake containing $\leq$ 55 percent moisture is formed on the vacuum filter test leaf; with a leaching solution containing $\sim$ 4.2 percent sodium (7 percent NaOHO, the wet cake would contain $\sim$ 2.3 percent sodium or 5.1 percent on a moisture-free (MF) basis. In theory, a first displacement wash should displace $\sim$ 90 percent of the original leaching solution, leaving only 0.23 percent sodium (0.51 percent MF). The second and third washes should displace 50 percent of any remaining solutions, leaving 0.12 percent (0.26 percent MF) after the second wash and 0.06 percent (0.13 percent MF) after a third wash. However, HTT coal is not an ideal solid. Rapid on-filter, vacuum-assisted, displacement washing tests showed the displacement rates for the first four washes were 40, 88, 38, and 24 percent. Wash liquor separation, without vacuum assistance, while approaching 40 percent displacement during the first wash and 60 percent on the second was was much too slow to allow practical application.(4) The poor washout by displacement stems from the low permeability of the filter cake due to (1) the presence of a small quantity of gluey slime, probably a calcium-sodium silicate compound; and (2) the compressive nature of the cake which requires the wash water to take a more tortuous path while encountering greater flow resistance.

Repulp Countercurrent Washing

Repulp washing consists of mixing the separated filter cake with wash liquor and refiltering. The process eliminates stratified regions in the cake that are washed at different levels, assures close contact of the wash liquor and the soluble materials, increases the rate of diffusional extraction, and (with proper media selection) can allow selective removal of slow-filtering slime. This method of washing can be incorporated into a washing circuit employing any type of separation equipment. It is especially suited for countercurrent "extraction" washing. Countercurrent extraction offers the most economical use of wash liquor, permitting (1) high sodium concentrations in the final extract sent to the evaporator and regeneration system and (2) high solute recovery from the treated coal with a minimal amount of fresh washwater. As applied to washing HTT coal, the washing scheme would include a number of separation stages in series.

Fresh washwater is mixed with the treated coal that has been most nearly exhausted of residual sodium. The filtrate from that operation is advanced progressively from one separation stage to the next until the most concentrated solution discharges from the separation stage where the fresh HTT coal slurry enters. Simultaneously, the separated solids are transferred from one stage to the next in the opposite direction, finally exiting from the freshwater washing stage. The finely ground solids could be leached by initial mixing followed by thickening and decantation or by filtration or centrifugation to separate the solids from the liquor. A simplified schematic of a countercurrent washing circuit is presented in Figure 1-1.(5) For the same example presented for displacement washing (i.e., a solution which renders a 55 percent moisture cake containing 5.1 percent MF sodium after initial separation), a countercurrent washing scheme with a washwater/coal ratio of 2 would reduce the sodium to 0.65 percent (MF) after three stages (87 percent removal) and 0.22 percent (MF) after five stages (96 percent removal). Thus, a five-stage ideal countercurrent washing circuit using 2/1 washwater-to-coal ratio would be approximately equivalent to an ideal displacement washing stage with two displacement washings (for the same

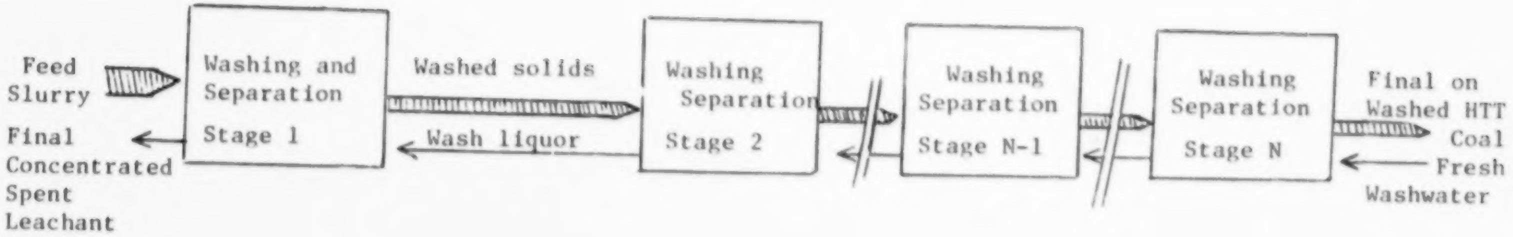

Feed
Slurry
Final
Concentrated
Spent
Leachant
Washing and
Separation
Stage 1
Washed solids
Wash liquor
Washing
Separation
Stage 2
Washing
Separation
Stage N-1
Washing
Separation
Stage N
Final on
Washed HTT
Coal
Fresh
Washwater

FIGURE 1-1. SIMPLIFIED COUNTERCURRENT WASHING CIRCUIT

washwater/coal ratio of 2). However, because of the much lower filtration rate obtained by displacement washing, nearly 40 times the number of filters will be required to effect the same separation.

Because of the difficulty in simulating a multistage countercurrent washing circuit, washing tests were conducted by repulp washing of the separated solid with fresh washwater rather than washing with filtrate from consecutive washings. The experimental data were compared to the predicted results and differences were accounted for by assigning an actual-to-theoretical stage efficiency used for downstream design and cost calculations.

APPENDIX 2

SEPARATION AND WASHING COST SIMULATION MODEL

The separation and washing cost simulation model is comprised of two parts. The first part calculates the residual dissolved sodium levels in the wash cake from countercurrent washing equations. The second part calculates the operating cost for various systems of filters or centrifuges used to separate the washed cake from the spent leachant.

PART I. COUNTERCURRENT WASHING

Calculation of the residual sodium level employs countercurrent washing equations. Solids, solute, and washing solution are brought into contact under perfect mixing conditions. The sodium in the liquid separated from the coal is at the same concentration as the sodium in the liquid retained with the filter cake. The ratio of the sodium in the n^{th} stage solution (Cn) to the sodium in the feed solution (Co) is calculated according to Equation (1).

$$\frac{Cn}{Co} = \frac{U^{n-1}}{A+1+B+B^2+\ldots B^{n-1}} = \frac{(1-B)(B^{n-1})}{A(1-B) + (1-B^n)} \qquad (1)$$

where:

Cn = lb dissolved sodium/lb coal free solution x 100

Co = lb dissolved sodium in the feed solution/lb coal free solution x 100

A = W/F

B = U/W

U = lb coal free solution in filter cake/lb dry solids

W = lb wash water/lb dry solids

F = lb coal free solution/lb dry solids

n = Number of washing stages.

The percent dissolved sodium in the final washed cake (Cf) is calculated by Equation (2).

$$Cf = U \times Cn = U \times Co \times \frac{U^{n-1}}{A+1+B+B^2+...+B^{n-1}} \equiv U \times Co \times \frac{(1-B)(B^{n-1})}{A(1-B) + (1-B^n)} \quad (2)$$

where:

Cf = (lb dissolved sodium in washed cake/lb dry solids) x 100. Therefore, the residual sodium is calculated for any number of n stages by setting the feed conditions, Co and F, and selecting the U corresponding to type of L/S separation device, and the wash water level W. For example, with a feed dissolved sodium level of Co = 3.9 percent sodium and 32 percent solids (F = 2.17 lb/lb), with a disc filter producing a filter cake containing 51 percent solids cake (U = 0.96 lb/lb) and wash water to dry solids level of W = 2, the dissolved sodium level of Cf after n = 5 stages is

$$Cf = (0.96 \frac{lb}{lb})(3.9) \frac{(1-0.48)(0.48^4)}{0.92(1-0.48) + (1-0.48^5} = 0.07 \text{ percent dissolved sodium}$$

$$A = W/F = 2/217 = 0.92 \qquad B = U/W = 0.96/2 = 0.48.$$

PART II. COST OF SEPARATION AND WASHING CIRCUIT

Part 2 of the model takes the dissolved sodium information and calculates the operating costs for the washing circuit. The total cost is comprised of the following eight components.

Cost for Makeup Sodium

The cost for makeup sodium is dictated by the quantity of sodium lost with the coal, defined in Equation (3).

$$CF_{sodium}(\$/\text{ton dry solids}) = \frac{Cf}{100} \frac{\text{Ton resid dissolved sodium left with HTC}}{\text{ton dry solids}}$$

$$+ \text{ Bound sodium, } \frac{ton}{ton} \times \frac{40 \text{ ton NaOH}}{23 \text{ ton sodium}} \times \frac{\$160}{\text{ton NaOH}} \qquad (3)$$

Cost for Treated Coal for Evaporator

The quantity of water to be evaporated (WEVAP ton/ton dry solids) equals the water added (W) minus the water removed with the coal (WRWC).

These terms are defined in equations (4) and (5).

$$\text{WRWC (ton water/ton dry solids)} = \text{U(ton/ton)} = \text{(100 - filter cake percent solids)/filter cake percent solids.} \quad (4)$$

$$\text{WEVAP (ton water/ton dry solids)} = \text{W(ton/ton)} - \text{WRWC(ton/ton)}. \quad (5)$$

The cost for the treated coal is presented in equation (6).

$$\text{COST}_{\text{T Coal}}(\text{\$/ton dry solids}) = \frac{\frac{0.4668 \text{ MMBtu}}{\text{ton water evaporated}} \times \text{WEVAP} \frac{\text{ton}}{\text{ton}} \times \text{Price HTC} \frac{\$}{\text{ton}}}{\frac{22.5 \text{ MMBtu}}{\text{Ton coal}} \times (0.83 \text{ efficiency factor})}$$

$$= 0.025 \times \text{WEVAP} \times \text{Price HTC}. \quad (6)$$

Since the price of treated coal is affected by the cost of separation and washing, the variability of the HTC price will be factored in later.

Cost for Utilities

Three forms of utilities are used in the separation and washing circuit: cooling water, process water, and electricity. Cooling water is employed in the evaporator used to remove the excess water added during washing. The cost is presented in equation (7).

$$\text{COST}_{\text{cooling water}}(\text{\$/ton dry solids}) = \frac{0.3211 \text{ MMBtu}}{\text{ton water vapor}} \times$$

$$\text{WEVAP} \frac{\text{ton water vapor}}{\text{ton dry solids}} \times 4.79 \frac{\text{Mgal}}{\text{MMBtu removed}} \times \frac{\$0.03}{\text{Mgal}} =$$

$$0.046 \times \text{WEVAP}. \quad (7)$$

Process water must be used to do the washing. This cost is presented in equation (8).

$$\text{COST}_{\text{process water}}(\text{\$/ton dry solids}) = \text{W} \frac{\text{ton water}}{\text{ton dry solids}} \times$$

$$\frac{.240 \text{ Mgal}}{\text{ton water}} \times \frac{\$0.20}{\text{Mgal}} = 0.048 \times \text{W}. \quad (8)$$

The cost of electricity is dependent on the type of L/S separation equipment; for vacuum filters the cost is

$$\text{COST}_{\substack{\text{electricity for}\\ \text{vacuum filters}}}(\$/\text{ton dry solids}) = (80 \times N_F\text{-No. of filters} + 96\ \text{Hp}) \times$$

$$0.7457\ \frac{\text{kW}}{\text{Hp}} \times \frac{1}{400\ \text{ton dry solids/hr}} \times \frac{\$0.03}{\text{kW-hr}} = (80 \times N_F\text{-No. of filters} + 96) \times 5.593 \times 10^{-5}. \quad (9)$$

for centrifuges the cost is

$$\text{COST}_{\substack{\text{electricity for}\\ \text{centrifuges}}}(\$/\text{ton dry solids}) = (2520 \times N\acute{c} - \text{No. of}$$

$$\text{centrifuge stages} + 96) \times (0.7457) \times (1/400) \times (0.03) =$$

$$(2520 \times N\acute{c} - \text{No. of centrifuge stages} + 96) \times 5.593 \times 10^{-5}. \quad (10)$$

The total cost for utilities is the sum of the costs for cooling and process water and electricity, equations (7), (8), (9), and (10).

Cost for Labor

The cost for labor is dependent on the number of L/S separation units required. One man can handle approximately six filters, therefore

$$\text{COST}_{\text{labor for filters}}(\$/\text{ton dry solids}) = (N_F\text{-No. of filters}) \times$$

$$\frac{1\ \text{man-hr/hr}}{6\ \text{filters}} \times \frac{1}{400\ \text{ton dry solids/hr}} \times \frac{\$10}{\text{man-hr}} = 4.167 \times 10^{-3}\ N_F \quad (11)$$

$$\text{COST}_{\text{labor for centrifuges}}(\$/\text{ton dry solids}) = (N\acute{c}\text{-No. of centrifuge stages}) \times$$

$$\frac{7.2\ \text{man-hr/hr}}{\text{centrifuge stage}} \quad \frac{1}{400\ \text{ton dry solids/hr}} \times \frac{\$10}{\text{man-hr}} = 0.18\ N\acute{c}. \quad (12)$$

The total labor cost is the cost of labor to operate the system of filters or centrifuges or any combination of filters and centrifuges, equations (11) and (12).

Cost of Capital Equipment

The major pieces of capital equipment involved in the separation and washing circuit are the L/S separation devices: evaporator, surge tank prior to the evaporator, pump to transfer the slurry from stage to stage, and wash water tanks. The capital cost of each item is estimated, then amortized to a \$/ton operating cost.

L/S Separation Devices. The L/S separation is accomplished in one of three devices: a rotary vacuum disc filter, a vacuum belt filter, or a screen bowl centrifuge. The number of L/S separation devices required for each stage is calculated as

$$\text{No. of disc filters} = \frac{\text{400 ton dry solids/hr}}{\text{filtration rate ton/hr}\cdot\text{ft}^2} \times \frac{\text{1 filter}}{3300\ \text{ft}^2} \times \frac{1}{\text{submergence factor} = .5} \times \frac{1}{\text{design factor} = .8} \times (\text{spare factor} = 1.15). \tag{13}$$

$$\text{No. of belt filters} = \frac{\text{400 ton dry solids/hr}}{\text{filtration rate ton/hr}\cdot\text{ft}^2} \times \frac{\text{1 filter}}{2400\ \text{ft}^2} \times \frac{1}{\text{effective surface factor} = 0.5} \times \frac{1}{\text{design factor} = .8} \times (\text{spare factor} = 1.15). \tag{14}$$

$$\text{No. of centrifuges} = \frac{\text{400 ton dry solids/hr}}{\text{centrifugation rate ton/hr}} \times (\text{spare factor} = 1.15). \tag{15}$$

For multiple stages the total number of each type of separator must be determined. As the cake is washed, the separation rate changes resulting in a different number of filters in each stage.

$$\text{COST}_{\text{disc filter}}(\$/\text{ton dry solids}) = \frac{\$653{,}400}{\text{filter, mix tank, and pumps}} \times$$

$$(N_{F_D}\text{-No. of disc filters}) \times (1.18\text{-contingency and fee factor}) \times$$

$$\frac{\text{Capitalization factor}}{(5.97\text{ yr})(300\text{ days/yr})(24\text{ hr/day}) \times (400\text{ ton/hr})} = \$653{,}400 \times N_F \times$$

$$6.858 \times 10^{-8}. \qquad (16)$$

$$\text{COST}_{\text{belt filter}} \; \frac{\$}{\text{ton dry solids}} = \frac{\$446{,}000}{\text{filter, mix tank, and pumps}} \times$$

$$(N_{F_B}\text{-No. of belt filters}) \times 6.858 \times 10^{-8}. \qquad (17)$$

$$\text{COST}_{\substack{\text{screen bowl}\\ \text{centrifuge}}} \; \frac{\$}{\text{ton dry solids}} = \frac{\$377{,}000}{\text{centrifuge, mix tank, and pumps}} \times$$

$$(\text{Nc-No. of centrifuges}) \times 6.858 \times 10^{-8}. \qquad (18)$$

Evaporator. The capital costs for the evaporator are scaled from a 300 ton/hr evaporator costing $4,212,000.

$$\text{COST}_{\text{evaporator}}(\$/\text{ton dry solids}) = (\$4{,}212{,}000) \times (400 \times \text{WEVAP}/300)^{0.8} \times$$

$$6.858 \times 10^{-8}. \qquad (19)$$

Surge Tank. The evaporator will operate continuously; in order to provide a steady continuous flow two surge tanks are provided before the evaporator. The cost of these surge tanks are again scaled from the cost of two holding tanks with approximately 3200 ton (800,000 gal) capacities each. A residence time of approximately 4 hours is provided in each tank, normally one would be empty while the other full.

$$\text{COST}_{\text{surge tank}}(\$/\text{ton dry solids}) = (\$260{,}000) \times (400 \times \text{WEVAP}/3200)^{0.66} \times$$

$$6.858 \times 10^{-8}. \qquad (20)$$

Pumps. The cost for pumps is scaled from an estimate of the cost for additional pumps required to transfer solution from stage to stage in a five filter system, when a wash water to coal ratio of W = 2 is employed.

$$\text{COST}_{\text{pumps}}(\$/\text{ton dry solids}) = (\$488{,}300) \times (W/2)^{1.2648} \times (6.858 \times 10^{-8}) \times \frac{N_F\text{-No. of filters}}{5} \qquad (21)$$

Wash Water Holding Tanks. The final capital item is the wash water holding tanks. The cost equation is based on the cost of a tank providing a 10 hr residence time with a W = 2.

$$\text{COST}_{\text{wash water tanks}}(\$/\text{ton dry solids}) = (\$207{,}000)(W/2)^{0.66} \times 6.858 \times 10^{-8}. \qquad (22)$$

The total amortized capital cost is the sum of all the capital costs, outlined in equations (16) through (22).

Moisture Penalty

The penalty for moisture is calculated by charging a cost equivalent to the Btu's required to vaporize excess water accompanying the HTC. Five percent moisture is considered the base case, that is, the moisture penalty for a 5 percent moisture coal is zero. The fraction of heating value lost due to excess moisture in the HTC, for any moisture content, is presented in equation (23) and illustrated in the Table 2.A-1.

$$Fx = \frac{\frac{x}{1-x}\,\frac{\text{lb water}}{\text{lb dry coal}} \times 1164\,\frac{\text{Btu}}{\text{lb H}_2\text{O}} \times \frac{2000\text{ lb}}{\text{ton}} \times \frac{1\text{ MMBtu}}{1 \times 10^6\text{ Btu}} - \begin{array}{l}0.123\text{ MMBtu/}\\ \text{ton to vapo-}\\ \text{rize the H}_2\text{O}\\ \text{in 5 percent}\\ \text{moisture coal}\end{array}}{22.5\text{ MMBtu/ton HTC}} \qquad (23)$$

TABLE 2-1. FRACTION OF COAL HEATING VALUE LOST DUE TO EXCESS MOISTURE IN HTC

X = Percent Moisture	$Y = \frac{\text{lb water}}{\text{lb dry coal}}$	Btu to Evaporate Water Accompanying 1 lb Dry Coal (= Y x 1164 Btu/lb)[a]	$\frac{\text{MMBtu}}{\text{ton dry coal}}$	$Z = \frac{\text{MMBtu}}{\text{ton}}$ 5% Moisture Coal	Fx = Fraction of Coal Lost (Z/22.5 MM Btu/ton)[b]
5	5/95 = 0.053	61.3	0.123	0	0
10	10/90 = 0.111	129.2	0.258	0.136	0.006
20	20/80 = 0.250	291.0	0.582	0.460	0.020
30	30/70 = 0.429	498.9	0.998	0.875	0.039
40	40/60 = 0.667	776.0	1.552	1.430	0.064
50	50/50 = 1.0	1164.0	2.328	2.206	0.098

(a) Assuming coal enters the boiler at 60 F and stack gases leave at 350 F, the required heat to vaporize 1 lb of water is ΔH - 1192-28 = 1164 Btu/lb.

(b) Five percent moisture HTC is assumed to have a heating value of 22.5 MMBtu/ton.

To obtain an equivalent amount of heat, 1/(1-Fx) tons of HTC (at the corresponding value of moisture content-X) must be burned. The moisture penalty is the cost of the excess HTC required

$$\text{Moisture Penalty} \times \frac{\$}{\text{ton dry solids}} = \frac{1}{1-Fx} - 1 \times (\text{Price of HTC}) =$$

$$\frac{(\text{Price of HTC})(Fx)}{(1-Fx)} \tag{24}$$

The only remaining item is the price of HTC. The cost is made up of the nonseparation and washing costs which equal \$30.94/ton, plus the costs for makeup sodium ($\text{COST}_{\text{sodium}}$), treated coal for the evaporator ($\text{COST}_{\text{T Coal}}$), utilities ($\text{COST}_{\text{utilities}}$), labor ($\text{COST}_{\text{labor}}$), capital ($\text{COST}_{\text{capital}}$), and moisture penalty ($\text{Cost}_{\text{M penalty}}$). However, the costs for treated coal for the evaporator and moisture penalty are functions of the price of HTC as noted in equation (25).

$$\text{PRICE}_{\text{HTC}} = \$30.94 + \text{COST}_{\text{sodium}} + (\text{COST}_{\text{T Coal}} = 0.025 \times \text{WEVAP} \times \text{PRICE}_{\text{HTC}}) + \text{COST}_{\text{utilities}} + \text{COST}_{\text{labor}} + \text{COST}_{\text{capital}} + \left(\text{COST}_{\text{M penalty}} = \frac{Fx}{1-Fx} \times \text{PRICE}_{\text{HTC}}\right). \tag{25}$$

The $\text{PRICE}_{\text{HTC}}$ can be solved from the equation by rearrangement to

$$\text{PRICE}_{\text{HTC}} = \frac{\$30.94 + \text{COST}_{\text{sodium}} + \text{COST}_{\text{utilities}} + \text{COST}_{\text{labor}} + \text{COST}_{\text{capital}}}{1.0 - (0.025 \times \text{WEVAP}) - \frac{Fx}{1-Fx}} \tag{26}$$

With the price of HTC established the cost of treated coal for the evaporator and the moisture penalty can be established.

Interest, Profit, and Income Tax

The last cost is for interest on borrowed capital, profit, and income tax. This cost is based on the capital investment and is

$$\text{COST}_{\text{interest, profit, income tax}}(\$/\text{ton dry solids}) = 1.46 \times \text{COST}_{\text{capital}}.$$

The total cost of the separation and washing circuit is the total of all the cost components discussed above.

MODEL SIMULATION

The cost model was used to simulate various possible washing circuits. The main variable was the type of L/S separation device employed. In each case, the filter cake percent solids was first set and then the wash water to coal ratio was set. With these fixed conditions, the model calculated the final dissolved sodium levels in the washed HTC cake and the cost for separation and washing. The wash water to coal ratio was then increased and the progress repeated. After W had been investigated over a 0.75 to 3 lb wash water/lb dry solids ratio (at 0.25 increments), the filter cake percent solids level was increased and the entire process repeated until a cake solids range of 46 to 58 percent solids (at 1 percent intervals) was investigated.

APPENDIX 3-A

SUPPORTING MATERIAL FOR LEACHANT REGENERATION:

PREPARATION OF LEACHANT

For this study, a Pittsburgh seam 8 coal from the Westland Mine, located in Washington County, Pennsylvania, was used. This mine taps one of the major seams in Pennsylvania with an estimated reserve of approximately 7-billion tons. The coal is a relatively high-sulfur, high-ash coal in the run-of-the-mine condition. However, it is subject to physical beneficiation (washing) to remove a portion of the sulfur and ash, but not to a level to permit direct firing without violating Federal Sulfur Emission Standards for New Sources. Analysis of this coal follows:

	Run-of-Mine Coal	Washed Coal
H_2O (%)	0	0.9
Ash	30.1	8.4
Sodium (%)	--	0.023
Total Sulfur (%)	3.61	2.04
Pyritic (%) (MAF)	2.38	1.32
Sulfate (%) (MAF)	0.32	0.04
Organic (%) (MAF)	0.91	0.68

A hydrothermal treatment unit was assembled in which the spent leachant and the first wash could be separated from the desulfurized coal under nonoxidizing conditions, i.e., without exposure of the liquors to atmospheric oxygen. This precaution was necessary in order to prevent oxidation of the sulfide sulfur contained in the leach liquors to thiosulfate, sulfite and/or sulfate sulfur since metallic compounds investigated for regeneration of the spent leachant will react only with the sulfide sulfur from the spent leachant. Another reason for taking this precaution was to gain further information on the reaction mechanism by which the sulfur is extracted from the coal by aqueous alkaline solutions. Previous work at BCL indicated that the reaction of pyritic sulfur with sodium hydroxide may proceed to produce soluble sodium sulfide. At least, the spent leachant was found to contain sulfide (Na_2S). However, literature reports indicated that oxidized forms of sulfur, for example $Na_2S_2O_3$, are formed in addition to the sodium sulfide. Both may be correct in that sodium thiosulfate may be formed in the hydrothermal treatment of coal, but is reduced to sulfide sulfur by the reducing action of some coals and/or the reducing gases--hydrogen and methane--formed during the desulfurization operation.

In the initial part of this research (an investigation using zinc oxide, $Fe(OH)_2$, $Fe(OH)_3$, reduced and activated Fe_2O_3, $Fe_2O_3 \cdot H_2O$, FeO(OH), Fe_3O_4, and FeO as regenerants), the washed coal, ground to 100 percent -48 mesh, was used.

Spent leachant was produced under the following conditions using a mixture of sodium hydroxide and lime as the desulfurization agents:

H_2O/coal ratio = 3
NaOH/coal ratio = 0.24
CaO/coal ratio = 0.098
Desulfurization temperature, C = 275
Retention time (at temperature), min = 10.

The operating procedure was as follows:

1. The reactants were mixed in a stainless steel liner and sealed in the 1-gallon autoclave.
2. The autocalve was purged several times with nitrogen to displace the atmospheric oxygen.
3. The reactants were heated to 275 C and held at temperature for 10 minutes.
4. The reaction product was cooled to 70-90 C.
5. Spent leachant was removed via pressure filtration. This was achieved by removing the leachant through a stainless steel filter which is part of the autoclave assembly. An over-

pressure of nitrogen was used to force the leachant through the filter medium.

6. The desulfurized coal was washed once while in the autoclave with deionized, degassed water.

After the above procedure, the desulfurized coal was removed from the autoclave. A portion was washed thoroughly to remove any residual spent leachant, dried, and analyzed to determine the degree of desulfurization and solubilization of the coal.

The results of analysis of leachant prepared in this way for total alkali, total sulfur, and sulfide sulfur, which are shown in Table 3, indicate that the majority of the sulfur was present in the spent leachant as sulfide sulfur. However, other forms were also present, accounting for approximately 20 to 37 percent of the total sulfur. They probably were in the form of oxidized sulfur species such as polysulfide, thiosulfate, sulfite, and/or sulfate.

TABLE 3-A.1 ANALYSIS OF SPENT LEACHANT

Experiment	Total Alkali[(a)] g/ℓ NaOH	Total Sulfur g/ℓ	Sulfide Sulfur g/ℓ
33018-5	62.6	4.31	2.70
33018-11	64.8	3.70	2.70
33018-19	N.A.[(b)]	N.A.	2.37
33018-21	N.A.	3.07	2.44
33018-25	∿ 60	2.89	2.25

(a) Includes sodium tied up in other forms such as sodium sulfur compounds.
(b) Not available.

For the subsequent research (an investigation of commercial iron oxides, soluble iron compounds, activated carbon, and ferrous carbonate as regenerants), the washed coal was ground to 70 percent -200 mesh. During grinding, handling, and storage, contact with air and thus oxidation of the coal surfaces was minimized as much as possible. A modified hydrothermal treatment unit and procedures also were used for this later work. The important modifications were:

1. The coal and sodium hydroxide were put into the autoclave in the dry state and the autoclave was sealed as rapidly as possible.
2. The autoclave and leachant receiver train were evacuated and flushed several times with pure, dry nitrogen.
3. The water to be used to make up the leachant was deoxidized by sparging with nitrogen, then was siphoned into the autoclave.
4. Leaching conditions:

   H_2O/coal ratio = 3.5
   NaOH/coal ratio = 0.36
   Desulfurization temperature = 275 C
   Retention time (at temperature) = 10 min.

The modified procedure and special handling decreased the concentrations of oxidized sulfur species, but did not eliminate them entirely, as was found to be possible in other previous research at Battelle using these procedures; typically 10 to 20 percent of the sulfur in leachant prepared under these conditions was of nonsulfidic species.

APPENDIX 3-B

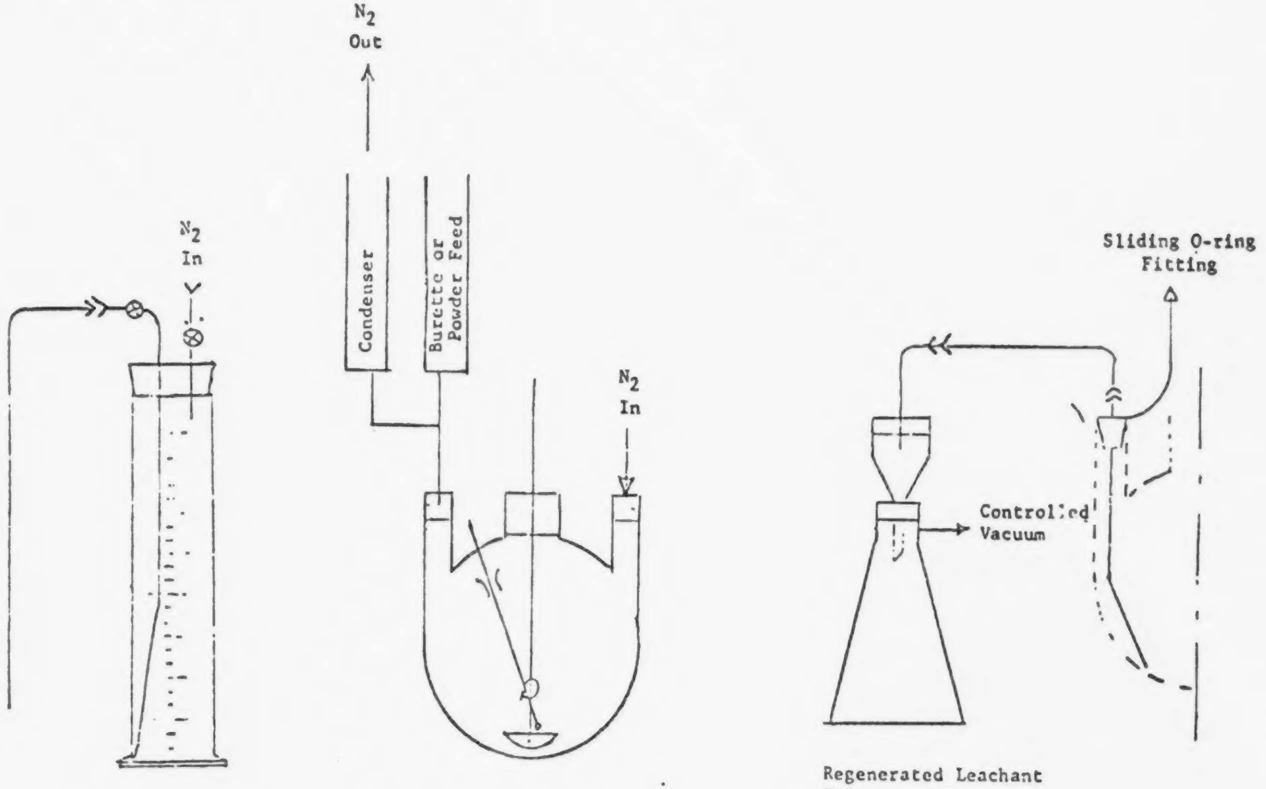
SUPPORTING MATERIAL FOR LEACHANT REGENERATION:

EXPERIMENTAL PROCEDURES: LEACHANT REGENERATION WITH ZINC COMPOUNDS

The need for an oxygen-free atmosphere when handling spent leachant was carried over into the regeneration operation. The arrangement of the spent leachant dispenser, regeneration reactor, the regenerated leachant filter and receiver are shown in Figure 3.B-1.

The recovered spent leachant was stored under nitrogen in a flash (Figure 3.B-1a) which also served as a dispenser of leachant in the preliminary experiments. The regeneration reactor (Figure 3.B-1b) was a 2000 ml round-bottom flask equipped with ground glass joints, stirrer, condenser, reagent feed (solution or powder), and a nitrogen inlet and outlet. The walls of the reactor were indented to provide turbulence during stirring. The vessel was heated by use of a heating mantle controlled by a variable transformer. Before filling with spent leachant, the vessel was evacuated and back-filled with nitrogen at least twice. With the flow of nitrogen continuing, the dispenser was pressurized with nitrogen and a known volume of spent leachant was forced into the reactor. The solution was then heated under a nitrogen flow to 80 C. Once at temperature, the appropriate amount of zinc was added either as a solution of sodium zincate in sodium hydroxide or as a weighed charge of powdered zinc oxide. Samples of solution were removed from the reactor at regular intervals after solids present had been allowed to settle. Samples used to follow the sulfide and zinc ion concentrations were extracted by means of a pipet and stored in stoppered nitrogen-filled flasks until analyzed. When the zinc was added as solution, both incremental and batch additions were made.

The sodium zincate solution was prepared by dissolving 37.7 g ZnO in about 400 ml of sodium hydroxide solution containing 142 g NaOH


N_2 Out
N_2 In
Condenser
Burette or Powder Feed
N_2 In
Sliding O-ring Fitting
Controlled Vacuum

Spent Leachant Dispenser

(A)

Regeneration Reactor

(B)

Regenerated Leachant Filter and Receiver

(C)

FIGURE 3.B.1 APPARATUS FOR REGENERATION OF SPENT LEACHANT

and then diluting to 500 ml. The resulting solution concentration was 0.926 mole/liter in ZnO and 7.1 moles/liter in NaOH. Zinc oxide powder was reagent grade while the pellets were 1/8-inch Zn-0103T catalyst from Harshaw Chemical Company (75 percent ZnO, the rest a combination of alumina, magnesia, calcia, and chromium oxide).

At the end of the reaction period, the solids were allowed to settle before removing the regenerated leachant. The leachant was filtered through a buchner funnel (Figure 3.B-1c) by creating a slight negative pressure in the receiver flash (which was purged with nitrogen first) and then forcing the solution from the reactor under nitrogen pressure through a tube. This tube was moveable and permitted rapid filtration of the leachant before the filter was coated with zinc sulfide. By following the liquid level as it fell, the amount of solids carried over was minimized. Once the separation was completed, the filtered, regenerated filtrate was stored under nitrogen suitable for leaching additional coal. The solid, mostly zinc sulfide, was washed from the reactor and the filter, was slurried for washing and was filtered again. The zinc sulfide, after air drying, and the regenerated leachant then were analyzed.

Pertinent to the regeneration is the variation of the solubility of ZnO at various sodium hydroxide concentrations. The solubilities of ZnO at 20, 40, and 100 C over sodium hydroxide concentration ranges of importance in this study are given in Figure 3.B-2. Here, it is noted that zinc solubility decreases with increasing temperature and decreases as the concentration of NaOH is lowered. Thus, at the NaOH concentration of about 2 moles/liter, normally used in the desulfurization step, the concentration of ZnO in solution could be about 0.2 mole/liter at 20 C and 0.08 mole/liter at 100 C ($\sim$16 g/ℓ and 6.5 g/ℓ, respectively), if excess zinc reagent were used.

In preparation for recycle experiments, the regeneration steps, liquid volumes, required analytical determinations, and laboratory procedure, were established as shown in Figure 3.B-3 so as to provide an insight into the information needed from the preliminary and shakedown experiments.

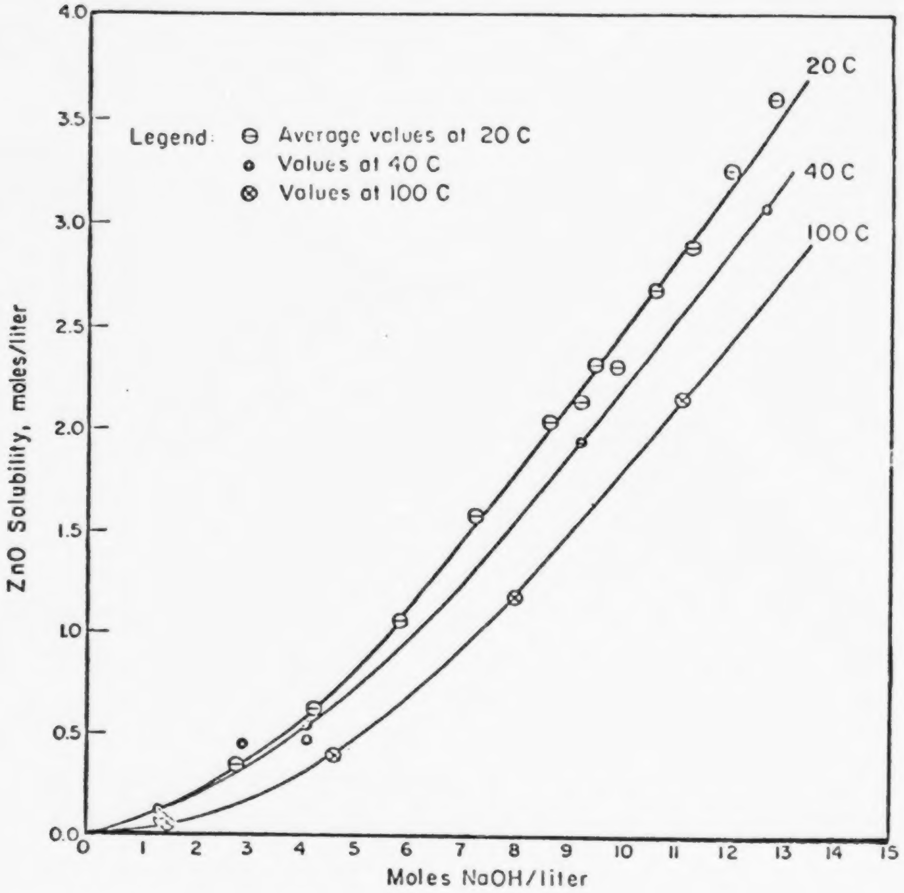
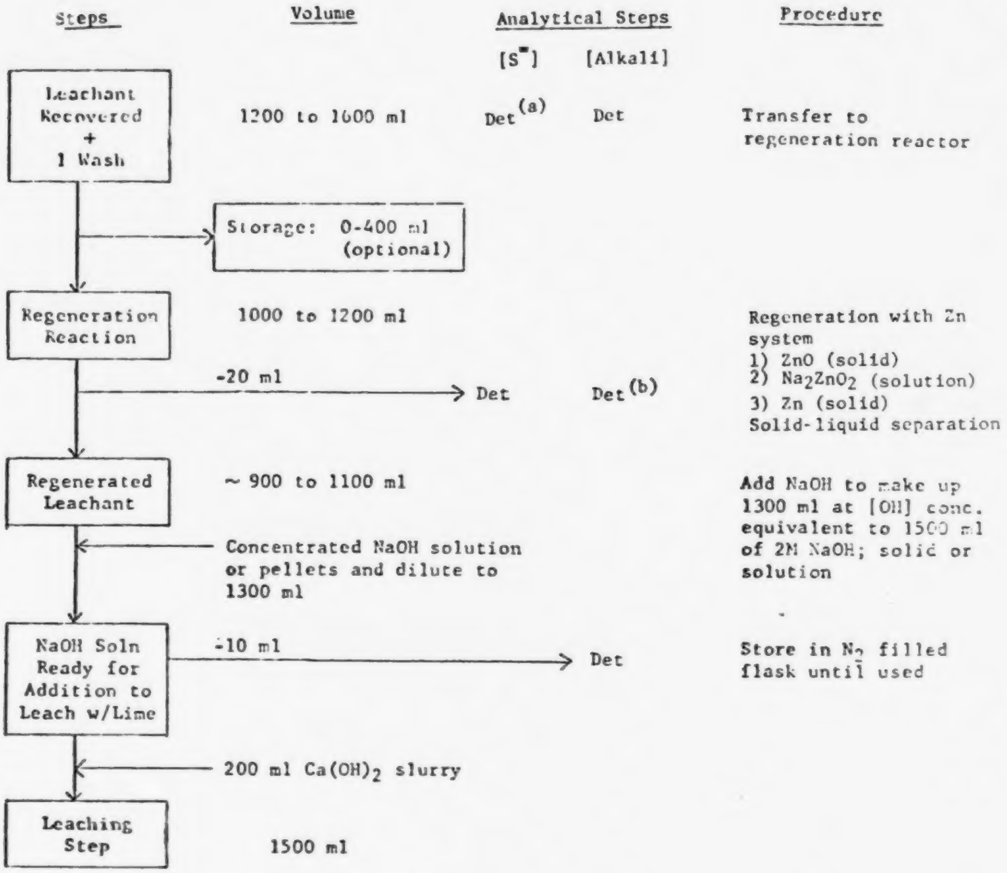


FIGURE 3.B-2. SOLUBILITY OF ZINC OXIDE AT VARIOUS SODIUM HYDROXIDE CONCENTRATIONS AT 20, 40, AND 100 C


Steps
Volume
Analytical Steps
Procedure
[S=]
[Alkali]
Leachant Recovered + 1 Wash
1200 to 1600 ml
Det(a)
Det
Storage: 0-400 ml (optional)
Regeneration Reaction
1000 to 1200 ml
-20 ml
Det
Det(b)
Regenerated Leachant
~ 900 to 1100 ml
Concentrated NaOH solution or pellets and dilute to 1300 ml
NaOH Soln Ready for Addition to Leach w/Lime
-10 ml
Det
200 ml Ca(OH)2 slurry
Leaching Step
1500 ml

Transfer to regeneration reactor

Regeneration with Zn system
1) ZnO (solid)
2) Na_2ZnO_2 (solution)
3) Zn (solid)
Solid-liquid separation

Add NaOH to make up 1300 ml at [OH] conc. equivalent to 1500 ml of 2M NaOH; solid or solution

Store in N_2 filled flask until used

(a)Det = Determine

(b)Zinc concentration also determined

FIGURE 3.B-3. SOLUTION HANDLING FOR LEACHANT RECYCLE

and then diluting to 500 ml. The resulting solution concentration was 0.926 mole/liter in ZnO and 7.1 moles/liter in NaOH. Zinc oxide powder was reagent grade while the pellets were 1/8-inch Zn-0103T catalyst from Harshaw Chemical Company (75 percent ZnO, the rest a combination of alumina, magnesia, calcia, and chromium oxide).

At the end of the reaction period, the solids were allowed to settle before the regenerated leachant was removed. The leachant was filtered through a buchner funnel (Figure 3.B-1c) by creating a slight negative pressure in the receiver flask (which was purged with nitrogen first) and then forcing the solution from the reactor under nitrogen pressure through a tube. This tube was moveable and permitted rapid filtration of the leachant before the filter was coated with zinc sulfide. By following the liquid level as it fell, the amount of solids carried over was minimized. Once the separation was completed, the filtered, regenerated filtrate was stored under nitrogen suitable for leaching additional coal. The solid, mostly zinc sulfide, was washed from the reactor and the filter, was slurried for washing and was filtered again. The zinc sulfide, after air drying, and the regenerated leachant then were analyzed.

Pertinent to the regeneration is the variation of the solubility of ZnO at various sodium hydroxide concentrations. The solubilities of ZnO at 20, 40, and 100 C over sodium hydroxide concentration ranges of importance in this study are given in Figure 3.B-2. Here, it is noted that zinc solubility decreases with increasing temperature and decreases as the concentration of NaOH is lowered. Thus, at the NaOH concentration of about 2 moles/liter, normally used in the desulfurization step, the concentration of ZnO in solution could be about 0.2 mole/liter at 20 C and 0.08 mole/liter at 100 C (∿16 g/ℓ and 6.5 g/ℓ, respectively), if excess zinc reagent were used.

In preparation for recycle experiments, the regeneration steps, liquid volumes, required analytical determinations, and laboratory procedure were established as shown in Figure 3.B-3 so as to provide as insight into the information needed from the preliminary and shakedown experiments.

Experimental Procedure

The ZnO powders or pellets were added batchwise to 500 ml of preheated (80 to 40 C) spent leachant. The suspension was stirred for two minutes and allowed to settle for six minutes before a 10-ml aliquot was removed for analysis of sulfide and zinc concentrations. This sample removal procedure was repeated over a period of one hour. Later it was found necessary to centrifuge the aliquots to assure removal of all suspended ZnS. (ZnS carryover would affect both $S^=$ and Zn values in the regenerated leachant.) In all operations, a nitrogen purge was maintained and all solutions were transferred under a nitrogen blanket and stored in stoppered nitrogen-purged vessels (including the centrifuge tubes).

Zinc oxide (reagent grade) with a surface area reported to be about 7 square meters/gram (equivalent to the best French Grade ZnO) was used in most of the experiments. However, a zinc oxide (pelletized) made by the American process with a surface area reported to be about 4 square meters/gram was used to determine the effect of the lower surface area. The amount of ZnO used in each experiment was determined by the concentration of sulfide ion in the spent leachant, the volume of the spent leachant charged into the regeneration vessel, and the Zn-to-S stoichiometry being investigated.

Additional experiments were carried out in a flow system. This entailed pumping the spent leachant through a bed of ZnO. Both the leachant and the ZnO were heated at 80 C. Flow rates of 5 milliliters per minute were used. The amount of zinc oxide in the bed ranged from 1 to 3 times the stiochiometric amount of sulfide ion present in the 500-ml charge. Bed contact times were in the order of 2 to 4 minutes. Samples for analysis were taken just as the first 15 ml passed through the reactor and then at the beginning of each subsequent 100 ml that passed through the reactor. Each sample was centrifuged and each experiment provided about five samples for each 500 ml charge of spent leachant processed.

Several preliminary screening experiments were carried out using zinc oxide powder and pellets and a solution of sodium zincate in sodium hydroxide.

From the preliminary data summarized in Table 3.B-1, zinc oxide in the form of a powder, pellet, or in solution is indicated to be an effective agent for the removal of sulfide sulfur from the spent leachant. In one experiment (33018-5), a slurry of ZnO (Zn/S ratio of 0.47) and the spent leachant was stirred at 26 C for 2 hours. The temperature was then increased to 80 C for 20 minutes, additional ZnO was added, and the slurry was heated at 80 C for an additional 20 minutes. Essentially complete (99.7 percent) removal of the sulfide sulfur was achieved.

Zinc pellets also appeared to be effective. However, it was concluded that a large excess of zinc oxide might be required because of the reduced surface area. Alternatively, it was speculated that a continuous system might be developed in which the spent leachant would be passed through a bed of pelletized ZnO.

TABLE 3.B-1. SUMMARY OF PRELIMINARY REGENERATION EXPERIMENTS WITH ZINC SYSTEM

Spent Leachant	Regeneration System	Reaction Conditions			Results
		Zn/S (mole ratio)	Temp., C	Time, Min	Reduction in Sulfide, %
33018-5a	ZnO powder	0.47	26	120	43.7
33018-5b		0.47	80	20	60.0
33018-5c		0.92	80	20	99.7
33018-11	Sodium zincate solution	0 to 1.0[(a)]	80	60[(b)]	94.0[(b)]
33018-11	ZnO, pellets	9.30[(c)]	26	6 days	93.0
33018-19	ZnO, pellets, fixed bed reactor[(d)]	18.30[(c)]	70	5 ml/min	44.0
33018-23	Sodium zincate solution	1.0	80	60	61.0
33018-23	ZnO powder	1.0	80	60	N.A.[(e)]

(a) Zincate added in increments.

(b) Maximum reduction. Seven-minute interval between 6 additions; total reaction time 60 minutes.

(c) The high Zn/S was taken because the leachant may not come in contact with all the ZnO in the pellet.

(d) Liquid downflow and N_2 upflow.

(e) N.A. - Not analyzed.

APPENDIX 3-C

SUPPORTING MATERIAL FOR LEACHANT REGENERATION:

LEACHANT DESULFURIZATION WITH COMMERCIAL IRON OXIDES

The commercial process for preparing iron oxides for pigment and magnetic applications constitutes a well established technology for producing iron oxide powders of controlled particle size and composition. To investigate the suitability of iron oxides prepared by this existing technology for the desulfurization of the coal leachant, experiments were conducted with two commercial iron oxides:

1. A high surface area commercial iron oxide, $Fe_2O_3 \cdot H_2O$ designated 2029-115-116 with a surface area of 107 m^2/g
2. A commercial yellow iron oxide, $Fe_2O_3 \cdot H_2O$ No. 300.

In the first experiment, in which a small excess of iron oxide and the shortest treatment time were used, good sulfur removal was observed (see first experimental results in Table 3.C-1). The total sulfur removal obtained, 77 percent and 3.83 g/ℓ, compared favorably with the best removal from spent leachant for which data were available in previous work (72 percent and 1.56 g/ℓ, Experiment 33179-23). The data show little decrease in sulfur concentration in the first hour and the lowest total sulfur value at the end of the experiment (i.e., after 3 hours)--thus suggesting the possibilities that (1) there may be an induction period involved in the sulfur-precipitation reaction, and (2) the sulfur concentration still may be decreasing after 3 hours.

In the subsequent experiments, higher excesses of iron oxide and longer reaction times were used. As can be seen in Table 3.C-1, the results are erratic, with many of the sulfur concentrations in the treated leachant samples being higher than those in the starting leachants.

Repeat analyses were run on selected samples as part of the investigation of the erratic results; the total sulfur values in parentheses in Table 3.C-1 are the results of a second set of analyses. Tests made subsequent to receipt of those unexpected results show that the commercial iron oxides contained appreciable concentrations of sulfate, with the concentration appearing to be significantly higher in the 2029-115-116 oxide which caused the much greater increases in treated-leachant sulfur concentrations. In addition, it is concluded from critical review of the work that, compared with the initial promising experiment, in the longer times required to filter the higher concentrations of iron oxides and sulfides from the leachant (in air), significant concentrations of sulfide sulfur may have been oxidized to (soluble) sulfate. Since the extent to which this occurred would depend on the variable time and surface area of exposure to air, the erratic results are understandable.

One additional experiment was run. In this experiment, the proportion of iron oxide was held near stoichiometric (as described in U.S. Patent 4,001,385 on the recovery of sulfur from pulping liquor), the high surface area $Fe_2O_3 \cdot H_2O$ was used, and a hydrogen atmosphere was maintained over the slurry.

Results showed that sulfide concentration was reduced from the initial 1.97 g/ℓ to 1.25 g/ℓ after 1 hour and to 1.22 g/ℓ after 3 hours of treatment (∿ 38 percent removal).

Attempts were made to wash the high-surface area iron oxide free of sulfate. After a number of repulping washes, sulfate tests indicated concentration remained high. Thus, it was concluded that this would not be feasible for a commercial coal process.

TABLE 3.C-1. SUMMARY OF EXPERIMENTS ON THE REGENERATION OF SPENT LEACHANT WITH IRON OXIDES

Sample/Experiment	Iron Oxide Leachant	Equivalents(a) of Fe Used	Temperature, F	Time, hr	Total Sulfur in Leachant, g/l	Total Sulfur Removed, %
70	$Fe_2O_3 \cdot H_2O$ 2029-115-116	3.4	180	0	5.00	
				1	4.95	
	Leachant 47-8-7			3	1.17	77
				3	1.17	77
72	$Fe_2O_3 \cdot H_2O$ 2029-115-116	12.7	180	0	2.54 (2.44)	
				2	3.36	
	Leachant 18-48-26			4	3.04	
				5	3.04 (3.20)	
74	$Fe_2O_3 \cdot H_2O$ #300 Yellow	20.4	180	0	1.59 (1.48)	
				1	1.18	
	Leachant 18-49-17			3	1.36	
				4	1.31	
				5	1.70 (1.52)	
75	$Fe_2O_3 \cdot H_2O$ 2029-115-116	20.4	80	0	1.59 (1.48)	
				1	2.60	
	Leachant 18-49-17			3	2.50	
				5	2.62	
76	$Fe_2O_3 \cdot H_2O$ #300 Yellow	20.4	80	0	1.59 (1.48)	
				1	1.99	
	Leachant 18-49-17			3	1.85	
				5	1.44	
77	$Fe_2O_3 \cdot H_2O$ 2029-115-116	13.7	120	0	2.36 (2.66)	
				1	3.13	
	Leachant 18-49-17			3	3.09	
				5	3.15	
80	$Fe_2O_3 \cdot H_2O$ #300 Yellow	16.5	180	0	1.97	
				1	1.81	
	Leachant 18-51-21 (10% by volume propanol propyl alcohol added to leachant)			3	1.92	
				5	1.84	

(a) Amount used was calculated on the basis of expected sulfur content. The values reported have been calculated on the basis of leachant sulfur content subsequently determined by analysis.

APPENDIX 3-D

SUPPORTING MATERIAL FOR LEACHANT REGENERATION:

EXPERIMENTAL PROCEDURES:
LEACHANT TRANSFER, TREATMENT, SAMPLING, AND ANALYSIS

For the exploratory experiments with iron compounds, iron hydroxides, and other iron-containing materials, experimental procedures were essentially the same as those used in the work with zinc compounds, except as noted.

Prior to the experiments with soluble iron compounds, leachant handling, treating, sampling, and analysis systems and procedures were modified to further minimize exposure to oxygen. These modified procedures were used in the experimental work with soluble iron compounds, activated carbon, and ferrous carbonate.

All transfers of leachant, such as from reservoir to treatment system and from treatment to analytical system, were made by use of hypodermic syringes through serum caps put on the vessels for the purpose.

The desulfurization treatments were carried out in closed vessels that had been evacuated and flushed several times with hydrogen, then filled with an atmosphere of the gas. Prior to use, the hydrogen was freed of oxygen by passing it through two catalytic units that converted oxygen present to water vapor by reaction with hydrogen. Magnetic stirring of the reaction mixture was used to eliminate the need for rotating seals.

Samples of the reaction slurry were withdrawn through serum caps into hypodermic syringes and likewise were transferred into serum-capped centrifuge tubes (that previously had been filled with purified hydrogen) for separation of liquid and solid. Samples of the treated leachant liquid similarly were transferred to the sulfide-analysis train, which previously had been sealed and flushed.

A standard iodometric method was used for the sulfide analysis. The sulfide was caused to evolve from the sample as hydrogen sulfide by use of strong mineral acid. The hydrogen sulfide was swept into a bubbler-type receiver by a flow of nitrogen where the sulfide was absorbed in zinc acetate solution as zinc sulfide.

The zinc acetate/zinc sulfide solution/slurry was acidified and the sulfide was oxidized to elemental sulfur with an excess of standard iodine solution. The excess of iodine then was back titrated with standard thiosulfate solution.

APPENDIX 3-E

SUPPORTING MATERIAL FOR LEACHANT REGENERATION:

LEACHANT DESULFURIZATION WITH SOLUBLE IRON COMPOUNDS: SODIUM FERRITE AND IRON NITRATE

SODIUM FERRITE TREATMENT

In the previous work with the use of iron hydroxides for leachant regeneration, it was found that freshly prepared hydroxide effectively precipitated 80 to 90 percent of the sulfide sulfur in the coal leachant. However, the effectiveness of the iron hydroxide as regenerated for reuse with boiling carbonated water was low, thus precluding economical recycling of the material.

Sodium ferrite solution ($NaFeO_2$) can be prepared by dissolving ferric oxide in 70 percent sodium hydroxide solution at 110 to 120 C. When the ferric solution is cooled or diluted, ferric hydroxide is precipitated. This reaction was seen to offer the possibility of recycling the iron compounds in the effective, freshly precipitated hydroxide form.

Exclusion of Oxygen. Prior to conducting these experiments, the systems for producing, treating, sampling, and analyzing the leachant were modified to improve exclusion of oxygen. These modified systems and procedures, which are described in Appendixes 3.A and 3.D, were used for these experiments and for indicated portions of the work discussed in ensuing sections of the report.

As a first step in investigation of the ferrite method, test reactions were run to confirm the chemistry. It was found that anhydrous red Fe_2O_3, jewelers rouge, could be dissolved in 70 percent sodium hydroxide at 110 to 120 C, and that dilution of the solution brought about precipitation of brown (hydrated) ferric hydroxide.

Experiments then were run on the desulfurization of coal leachant with the sodium ferrite. In these experiments, 7.75 g of

$Fe_2O_3 \cdot H_2O$, which had been precipitated from ferric nitrate by neutralization with ammonia, was dissolved in 50 grams of 70 percent sodium hydroxide solution in the closed reactor system. This quantity of iron is about 9.7 times the quantity required to react with the sulfide iron in 150 ml of leachant that contains about 2 grams/liter of sulfide. One-hundred-fifty milliliters of coal leachant was then introduced into the reactor under anaerobic conditions to dilute and react with the sodium ferrite solution. In the first experiments, reaction temperature was held at about 190 F, in the range reported to give complete reaction of ferric iron and sulfide (U.S. Patent 4,001,385). Subsequent experiments were run at room temperature.

Results of the experiments with sodium ferrite, which are given in the first part of Table 3.E-1, have been corrected for the dilution that occurred when the ferrite-containing sodium hydroxide solution and the leachant were combined. The results, which are thus based on the initial volume of leachant, show that the desulfurization was more effective at room temperature than at 190 F, and that about 75 percent of the sulfide sulfur has been precipitated as ferrous sulfide and removed from the leachant.

In continued experimentation, shorter treatment times and various iron oxide concentrations were investigated. Results of these experiments show that:

1. When ∿ 10 or more equivalents of iron are used, the sulfur-precipitation reaction is essentially complete in 15 to 30 minutes at room temperature.
2. Sulfide concentration was down near that found to be satisfactory for leachant recycle (1975 Summary Report on Hydrothermal Coal Processing, September 1, 1976).
3. Iron concentrations of approximately 1 and 2 equivalents were not effective.

Comparison of the analytically determined concentrations of sulfide sulfur and total sulfur indicates that some sulfide sulfur had been oxidized in the course of the treatment processing. This is believed to accompany

TABLE 3.E-1. SUMMARY OF EXPERIMENTS ON LEACHANT DESULFURIZATION

Experiment	Regenerant	Leachant Treated	Equivalents of Fe Used	Temp, F	Time, hr	Sulfide Present, g/1	Sulfide Removed, %	Total Sulfur Present, wt %	Total Sulfur Removed, %
		33018-54-17				1.82		0.16[a]	
018169	$Fe_2O_3 \cdot H_2O$ precipitated from $NaFeO_2$ solution	33018-54-17	10.4	75	1	0.16	91	0.09	44
					2	0.16	91	--	--
018-73	$Fe_2O_3 \cdot H_2O$ precipitated from $NaFeO_2$ solution	33018-54-17	22.4	71	1/4	0.224	88	--	--[b]
					1/2	0.192	89	0.12	25
					1	0.384	79	--	--
					2	0.192	89	--	--
018-77	$Fe_2O_3 \cdot H_2O$ precipitated from $NaFeO_2$ solution	33018-53-18	2.22	70	1/4	--	--	--	--
					1/2	0.99	63	--	--
					1	0.70	74	--	--

(a) 1.78 g/1, assuming solution has specific gravity of 10 percent NaOH solution.

(b) Possibility of leakage of air into the system was discovered following the experimental run.

reduction of a portion of the iron from the ferric to the ferrous state. No firm data have been obtained on the effect of the presence of oxidized forms of sulfur in the leachant.

Intermediate proportions of iron oxide should be investigated and additional data should be obtained with effective proportions at short treatment times.

One experiment was run on recycle by the ferrite method. Data on this experiment which are given in Table 3.E-2 (original regeneration-Experiment 018-84; regeneration with recycled iron oxide-Experiment 018-85) show the typical 90 percent sulfide removal with the fresh material and 80+ percent removal with the recycled material. Performance of the recycled material was close enough to that of the initial to warrant additional experiments. In this run, the yield of iron oxide material from the recycle treatment was about 50 percent, with losses presumably being due to handling as well as solubilization in the strong caustic soda solution; thus, the typical yield should be determined in the additional experiments.

In view of the promising results, a cursory cost evaluation was made for the ferrite recycle process. The data which are summarized in Table 3.E-3 indicate that the probable cost will be higher for the ferrite process than for the carbonate process.

IRON NITRATE TREATMENTS

The use of soluble iron compounds offers the possibility of getting high concentrations of iron ions in solution, at least for a short period. Another aspect of the use of soluble iron compounds is that the hydroxides are freshly precipitated in the sodium hydroxide leach solution that is to be desulfurized. Iron nitrates were used to investigate the potential effects on regeneration of highly soluble iron compounds.

Solubility data indicate that the concentration of iron in solution in the basic coal leachant solutions will be orders of magnitude greater if the iron is in the ferrous, rather than the ferric, state. Solubility product constants for the hydroxides are 8×10^{-16} and 3×10^{-36} for ferrous and ferric, respectively; hence, in 2.5 normal hy-

TABLE 3.E-2. EXPERIMENT ON LEACHANT DESULFURIZATION WITH RECYCLED IRON VALUES

Experiment	Regenerant	Leachant Treated	Equivalents of Fe Used	Temp, F	Time, min	Sulfide Sulfur, g/1	Sulfide Sulfur Removed, %	Total Sulfur, g/1	Total Sulfur Removed, %	Remarks
018-84	Fe_2O_3 x H_2O precipitated from ferric nitrate solution	018-44	24.3	70		2.33				
					30	0.78(a)	67			(a) Sample inadvertentlv not acidified prior to titration
					60	0.20	91			
018-85	Fe_2O_3 x H_2O(b) precipitated from ferrite solution	018-44	24.7	70		2.33				
					30	0.39	83			(b) Regenerant from 018-84 recycled by ferrite method
					60	0.41	82			

TABLE 3.E-3. CURSORY COST EVALUATION OF FERRITE PROCESS

Process Description

(1) Dissolve waste iron oxide in 70 percent NaOH solution at 120 C as the ferrite.

(2) Precipitate active hydrated iron oxide by dilution and cooling.

(3) Separate the iron oxide from the NaOH solution by filtration (reconcentrate the NaOH solution for reuse).

(4) Slurry contact the spent coal leachant with the iron oxide to desulfurize the leachant.

(5) Separate the regenerated leachant and the iron oxide/sulfide by filtration.

(6) Leachant to re-use; iron oxide/sulfide to disposal.

Assumptions

Cost of waste iron oxide	$.01 per lb.
Cost of sodium hydroxide	$.16 per lb.
Cost of water evaparation	$.01 per lb.
Specific heat of solution	∿1

Estimated Cost per Ton of Coal Processed

Cost Item	Use of (Ideal) Equivalent Proportion of Iron Oxide	Use of (Required) 3 Times Equivalent Proportion of Iron Oxide
Waste iron Oxide @ 1¢/lb	$1.00	$ 3.00
Sodium hydroxide @ 16¢/lb	4.80	14.40
Solution reconcentration	1.70	5.10
Solution heatup (20 to 120 C)	1.11	3.33
Iron oxide/sulfide disposal*	.50	1.50
	$9.11	$27.33

*Blue sky estimate.

These costs are higher than projected costs for carbonate regeneration of leachant.

droxide solutions, equilibrium concentrations of ferrous and ferric iron would be about 1 x 10^{-16} and 2 x 10^{-37} gram-ions per liter, respectively, indicating the ferrous iron solubility to be greater by about 10^{20}. To investigate the possibility of exploiting this, experiments were undertaken on the use of ferrous iron. Experiments also were carried out with ferric nitrate.

Ferrous nitrate in solution was prepared by agitating iron (powder) in ferric nitrate solution under anaerobic conditions to bring about the reaction $Fe^\circ + Fe^{+3} \rightarrow 2Fe^{+2}$. The ferrous nitrate solution then was introduced into, and reacted with, the leachant solution under anaerobic conditions.

Results of the first two experiments (018-66 and -68, Table 3.E-4) indicated that the ferrous solution was very effective, removing about 70 to 80 percent of the sulfide sulfur from the leachant.

Additional experiments conducted with ferric nitrate, along with the initial experiments with the ferrous compound, were intended to investigate the relationship between desulfurization and the proportion of iron oxide used. The results, which are plotted in Figure 3.E-1, indicate that more than 20 equivalents of iron should be used to obtain good desulfurization of the leachant.

Several experiments were carried out in which sodium formate was added to investigate the possibility that formate as a reducing agent would hold the sulfur in the sulfide state and thus improve the efficiency of the desulfurization reaction. Results of these experiments, along with others completed in this month, also are given in Table 3.E-5. In the first, Experiment 018-79, the formate was added initially and was present throughout the treatment. In the second, Experiment 018-80, the formate was introduced after 70 minutes of treatment time had passed, and a sample was taken for analysis 20 minutes later. The results of the sulfide analyses indicate that no beneficial effect was produced by use of the formate.

Overall, results confirm that when sufficient proportions of iron oxide are used, good sulfide removal (approximately 90 percent) is obtained by use of short treatment times (30 minutes or less) at room temperature. However, an economical and environmentally acceptable process for the recycle of iron values would be required for use in a commercial regeneration process.

TABLE 3.E-4. SUMMARY OF EXPFRIMENTS ON LEACHANT DESULFURIZATION

Experiment	Regenerant	Leachant	Equivalents of Fe Used	Temp, F	Time, hr	Sulfide Present, g/l	Sulfide Removed, %	Total Sulfur Present, wt %	Total Sulfur Removed, %	Remarks
	33018-54-17	018-54-17								
018-66	$Fe(NO_3)_2$	018-54-17	1.0	75	1-2/3	0.58	68	0.19		
018-68	$Fe(NO_3)_2$	018-54-17	410	75	2	0.37	80	--	-	
		018-53-18				2.7		--	-	
018-76	$Fe(NO_3)_3$	018-53-18	0.74	70	1	1.7	37	0.30	-	
								0.22	-	
018-78	Fe_2O_3 x H_2O precipitated from ferric nitrate solution	018-54-17	7.8	70		1.62				
					1/2	0.77	52			
					1	0.52	68			
018-79	Fe_2O_3 x H_2O precipitated	018-44	24.3	70		2.33				*Formate added; 2 times that required to reduce all sulfur from $S_2O_3^{--}$ state
018-80	Fe_2O_3 x H_2O precipitated from ferric nitrate solution	018-44	24.3	70		2.33				
					1/2	--				
					1	0.24	90			
					1-1/6*					
018-84	Fe_2O_3 x H_2O precipitated from ferric nitrate solution	018-44	24.3	70		2.33(a)				**30-minute sample lost
					1/2	0.78(a)	67			(a) Sample inadvertentlv not acidified prior to titration
					1	0.20	91			

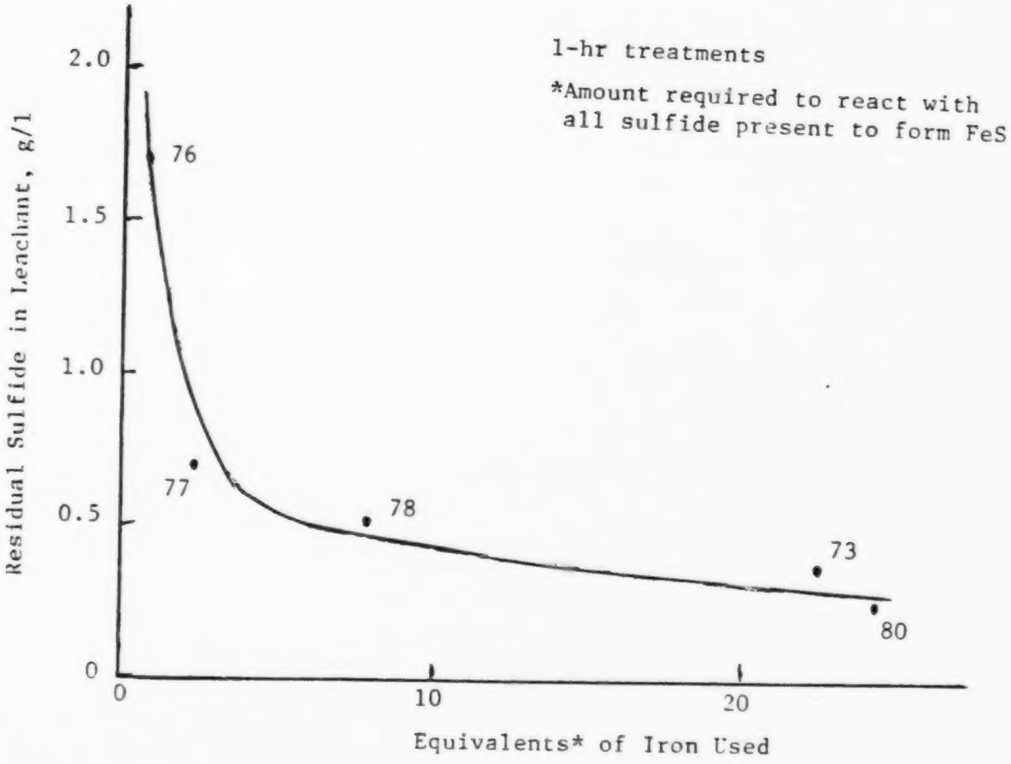


FIGURE 3.E-1. RESIDUAL SULFIDE IN TREATED LEACHANT VERSUS PROPORTION OF IRON OXIDE USED

APPENDIX 3-F
SUPPORTING MATERIAL FOR LEACHANT REGENERATION:
OTHER LEACHANT REGENERATION APPROACHES

ACTIVATED CARBON

It is known from other technology that both ionic and molecular species can be adsorbed onto the surface of activated carbon from aqueous solution. The solution is thus purified with respect to the adsorbed species. The "impurities" can then frequently be removed from the carbon thermally or by washing, thus making the carbon suitable for re-use.

Initially, two experiments were conducted on the desulfurization of spent leachant in which the leachant was passed through columns packed with granular (∿12 x 30 mesh) activated carbon at room temperature. The results, which are summarized in Table 3.F-1, indicated that good desulfurization might be obtainable by use of this relatively simple and potentially low-cost method. The analytical results show that 67 percent and 60 percent total sulfur removal were obtained in samples of the first leachant to pass through the column, with a relatively low residual sulfur concentration of 0.78 g/l indicated in both experiments. The results of an initial analysis of the leachant for sulfide sulfur indicated about 0.9 g/l of the sulfur to be nonsulfidic (and therefore in an oxidized state); however, as will be discussed, it was found necessary that the analytical system and procedures be modified and the analysis repeated.

Short runs with low volumes of throughput were made in these initial, exploratory experiments. Therefore, nothing was known at that time regarding results obtainable when significant volumes of leachant were processed through a column or bed of carbon. The results of Experiment 81 indicate that residual sulfur concentration in the processed leachant was dropping through what may have been an initial "column conditioning" portion of the run. Likewise, nothing was known regarding the sulfur-adsorption capacity of the carbon or of the relative suitability of various carbons.

TABLE 3.F-1. SUMMARY OF EXPERIMENTS ON THE REGENERATION

Experiment/	Activated Carbon	Volume/Length of Column, cm^3/cm	Volume of Leachant Processed, ml	Total Sulfur in Leachant, g/l	Total Sulfur Removed, %
78	#400	174/77	$0^{(a)}$	2.36 (2.66)	
			25	0.78	67
	Leachant 18-49-17				
81	#400	345/152	$0^{(a)}$	1.97	
	Leachant 18-51-21		~30	1.25	
			~100	0.78	60

(a) Spent leachant before treating.

It was known from the previous work that the leachant contained oxidized sulfur species, presumably resulting from the presence of adsorbed oxygen or of oxygen-containing groups in the coal that was leached. Therefore, sulfide sulfur analyses of samples of both starting and treated leachant were planned, along with the determination of the total sulfur concentrations, to be used in interpretation of the results of the experiments.

A number of additional experiments were run on the adsorption of sulfur species on the activated carbon. These experiments were carried out using synthetic leachants to make possible determinations of the extent of adsorption of the individual types of sulfur species. Solutions containing sulfide sulfur were made up and fed into the adsorption column under inert conditions to preclude oxidation. The carbon-packed columns were degassed (deoxidized) prior to use by high temperature treatment in flowing nitrogen and hydrogen.

Results of the experiments, which are given in Table 3.F-2, show highly effective adsorption of sulfide in an initial portion of each run (Experiments 79-97, -99, -100, 18-58A) followed by relatively rapid de-

TABLE 3.F-2. SUMMARY OF CARBON ADSORPTION EXPERIMENTS

Experiment	Composition of Synthetic Leachant	Conditions of Carbon Degassing	Rate of Leachant Throughput, ml/min	Throughput Volume Interval of Sample, ml	Analysis of Sample			Remarks
					S^{--}, g/l	Total S, g/l	Na, g/l	
79-97	40 g/l NaOH, 2.5 g/l S^{--} as Na_2S	N_2 flow at 800 C, 2 hr	10	Starting material	2.34	--	--	
				75-150	0.096	--	--	96% S^{--} removal
		Triple, 150 cm column		225-300	0.032	--	--	98+% S^{--} removal
				375-450	1.73	--	--	26% S^{--} removal
				825-900	1.92	--	--	18% S^{--} removal
				1300-1400	2.08	--	--	11% S^{--} removal
79-99	40 g/l NaOH, 2.5 g/l S^{--} as Na_2S	N_2 flow at 800 C, 2 hr	10	Starting material	2.34	--	--	
				0-75	0.096	--	--	96% S^{--} removal
		Triple, 150 cm column		150-225	0.032	--	--	98+% S^{--} removal
				225-300	1.28	--	--	45% S^{--} removal
				700-8--	1.60	--	--	32% S^{--} removal
79-100	40 g/l NaOH, 2.5 g/l S^{--} as Na_2S	N_2 flow at 800 C, 2 hr: then H_2 flow at 800 C, 2 hr	10	Starting material	2.34	--	23	
				0-100	0.03	0.16	20.2	98+% S^{--} removal
				1650-1750	2.21	2.35	22.2	5% S^{--} removal
18-57A	80 G/l NaOH, 2.5 g/l S as Na_2SO_3	None Single, 50 cm column	6	200-300 -- Strong positive qualitative test for sulfite				
18-57B	80 g/l NaOH, 2.5 g/l S as Na_2SO_4	None Single, 50 cm column	6	Starting material -- 7.5 g/l sulfate 200-300 -- 7.51 g/l sulfate				
18-58A	80 g/l NaOH, 2.5 g/l S as Na_2S	None, single, 50 cm column, countercurrent air flow	6	250+ -- Polysulfide yellow				
18-58B	80 g/l NaOH 2.5 g/l S as $Na_2S_2O_3$	None, single 50 cm column, countercurrent air flow	6	200-300 -- Strong positive qualitative test for $S_2O_3^{--}$				
18-58B	80 G/l NaOH 2.5 g/l S as $Na_2S_2O_3$	None, single, 50 cm column, countercurrent air flow	6	200-300 -- Strong positive qualitative test for $S_2O_3^{--}$				

crease of adsorption as the column appeared to become saturated. The drop-off of adsorption was accompanied by the appearance of yellow polysulfide in the solution.

The results of Experiments 18-57A, -57B, and -58B indicate that oxidized sulfur species (sulfite, sulfate, thiosulfate, respectively) were not adsorbed effectively.

Overall, results of the experiments indicated that:

1. sulfide can be adsorbed effectively from the used leachant (95-98 percent) by use of activated carbon, but the capacity of the carbon used is small (∿ 0.5 g carbon/ml of 2.5 g S/l leachant),
2. the carbon does not adsorb sulfate sulfur and other oxidized sulfur species, and
3. the carbon adsorbs only a small proportion of the sodium from the leachant.

LEACHANT DESULFURIZATION BY ELECTROLYSIS

Tripolar-Wiped Electrode System

An electrolytic process would provide a low-cost and convenient means of desulfurizing the leachant prior to recyclé. The theoretical quantity of electrical power required to "plate out" the sulfur extracted from typical eastern bituminous coal is about 15 kWh per ton, suggesting a cost under $1.00 per ton. In addition, it should be possible to carry out the electrolysis without otherwise modifying the composition of the leachant.

It has been shown that sulfide can be "plated out" of acidic solution if a tripolar-wiped electrode system is used to continuously remove the current-limiting elemental sulfur deposit from the anode*. It has been observed in previous work here that a film of elemental sulfur can be deposited in a similar way from the basic leachant solutions.

To investigate this electrolytic approach, a three-compartment electrolytic system was set up. The first compartment contained the coal leachant solution and the active anode and cathode. The second compartment contained a sulfur solvent, and the third contained a wash solution to remove residual sulfur solvent. A triple anode was used, with the system constructed to permit each of the anode parts to be placed successively in the three compartments. The rotation was carried out manually and untreated stainless steel electrodes were used for these exploratory experiments. Nominal potentials of 1 to 1.5 volts were used and about 25 electrolytic cycles were employed in each experiment. Toluene and ethanol were used as solvents.

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* Farooque M. and Fahidy, T.Z., J. Electrochem Soc., 124, 1191 (1977).

The results, which are given in Table 3.F-3, show that about 30 percent of the sulfide sulfur was removed from the leachant in the first experiment. Considering the relatively crude nature of the experiment, this is an encouraging result. It is possible, however, that sulfur was oxidized to higher states,which remained in the solution (rather than being deposited as elemental sulfur). Total sulfur analyses must be run to check on this.

Iron-Screen Anode System

Experimental investigation of a different type of electrolysis was undertaken using both synthetic and real spent leachant. The experiments were conducted in nitrogen-blanketed beakers (containing 150 ml of solution). An iron screen was used as the anode (positive electrode) and iron strip was used on the cathode (negative electrode). The iron screen anode was used with the expectation that the sulfur would be removed from the system as iron sulfide. Limiting voltages and current were supplied by a D-C source. Typically, the voltage limit was set at 2 volts while the current was limited to 0.2 ampere. Electrolysis usually ran for 1 to 2 hours at either room temperature or 80 C. The anode screen was washed, dried, and weighed before determining the amount of FeS formed by the measuring H_2S evolved during acid treatment of the anode screen.

While reductions in the sulfide sulfur content of the synthetic and real spent leachants were observed (see Table 3.F-4), corresponding reductions were not achieved in the total sulfur content. It is possible that during electrolysis, the sulfide sulfur was converted to elemental sulfur which in turn dissolved in the spent leachant to form

TABLE 3.F-3. SUMMARY OF EXPERIMENTS ON LEACHANT DESULFURIZATION

Experiment	Regenerant	Leachant	Equivalents of Fe Used	Temp, F	Time, hr	Sulfide Present, g/l	Sulfide Removed, %	Total Sulfur Present, wt %	Total Sulfur Removed, %	Remarks
018-63	Electrolysis	33018-54-17	-	75	-	1.26	31	--	-	26 electrolytic cycles
018-65	Electrolysis	33018-65-17	-	75	-	1.47	19	--	-	25 electrolytic cycles

TABLE 3.F-4. LEACHANT REGENERATION BY ELECTROLYSIS

Experiment	Electrolysis Conditions				Weight Change, mg		Characteristics of Spent Leachant Treated			Characteristics of Regenerated Leachant		
	Current, amperes	Volts, D.C.	Temperature, C	Time, minutes	(+) Anode	(-) Cathode	Type	S_{Total} g/1	$S_{S^=}$ g/1	S_{Total} g/1	$S_{S^=}$ g/1	Percent Sulfide Reduction
33179-42	0.2	0.1	27	30	+27.7	+0.7	SYL[a]	2.58	2.53	--	2.46	2.5
				90						--	2.43	3.8
33179-44	0.2	0.6-0.9	27	29	+26.0	-1.2	SYL	2.58	2.53		2.35	9.3
				133							1.94	33.0
				168						2.45[b] 2.44[c]	1.63	37.0
33179-48	0.2	0.9	27	30	+23.9	-0.4	SL[a]	2.47	2.07		1.70	18.1
				60							1.44	30.4
				90							1.18	42.8
				150						2.34	0.94	54.4
33179-50	0.2	0.6	80	10	+37.7	-0.1	SL	2.47	2.07		1.83	11.6
				30							1.63	21.3
				60							0.50	27.5
				80						2.37	1.28	38.2
33179-54	0.4	1.0	27	10	+32.0	--	SYL	2.58	2.53		2.18	16.0
				30							1.79	30.8
				60						2.27[b]	1.70	34.5

(a) SYL, synthetic leachant; SL, spent leachant from coal desulfurization.
(b) Synthetic leachant solution turned yellow due to polysulfide formation from S° and Na_2S.
(c) Reduced iron oxide added in attempt to remove polysulfide.

sodium polysulfide according to the reaction:

$$S^{=} \xrightarrow{\text{electrolysis}} S^{\circ} + 2e$$

$$XS + Na_2S(aq) \longrightarrow Na_2S_X(aq) \ .$$

Apparently, this may have been the predominate reaction. During the electrolysis, the synthetic spent leachants gradually turned yellow. There was a slight increase in the weight of the anode, but not in correspondence to the decrease in the sulfide sulfur concentration. The results of analysis of the deposit on the anode suggested only part of the material was FeS. Also, the amount of sulfur present as FeS did not account for all of the weight gained by the anode as shown in Table 3.F-5. However, there was reasonable correlation between the weight gained by the anode and the change in the total sulfur in solution. Any difference might be attributed to the codeposition of elemental sulfur in the anode deposit.

Further work will be required to assess the viability of electrolysis for regeneration of the spent leachant. It might be that the formation of the polysulfide can be prevented by the use of a moving belt of an iron anode with a high surface area. This technology is being used by the electroplating industry for metals recovery from waste streams.

TABLE 3.F-5. COMPARISON OF ELECTRODE WEIGHT GAIN TO THE AMOUNT OF SULFIDE FORMED AND CHANGE IN TOTAL SULFUR IN SOLUTION

Experiment	Weight Gain Iron Anode, mg(a)	Sulfur as FeS on Anode, mg	Change in Total Sulfur in Solution, mg
33179-44	26.0	12.8	20
33179-48	23.9	6.5	20
33179-50	37.7	10.1	15
33179-54	∿32	9.0	47

(a) Weight gain assumed to be sulfur capture.

Electrolytic Preparation of Iron Hydroxide

In an open-ended process, the sulfide containing iron hydroxide would be discarded. Such an approach would require that fresh ferric hydroxide be supplied for each spent leachant regeneration cycle. One method of preparing ferric hydroxide is to treat soluble ferric salts with sodium hydroxide. However, material prepared in this manner would be contaminated with the anion originally present in the ferric salt. Thus, these anions would build up in the regenerated leachant and the effect would be counter to the objectives of the regeneration scheme. Thus, the preparation of iron hydroxide by the anodic dissolution of iron in sodium hydroxide solutions was investigated. By this technique, iron ions and hydrogen would be formed according to the reactions:

$$Fe \rightarrow Fe^{++} + 2e \cdot \text{(Anode Reaction)} \qquad (1)$$

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \cdot \text{(Cathode Reaction)}. \qquad (2)$$

When sodium hydroxide solution was used, no significant yield of iron hydroxide was obtained. When sodium chloride (which is used in the electrochemical machining of steel) was used in place of sodium hydroxide, rapid dissolution of iron occurred to form a suspension of ferrous-ferric hydroxide in the sodium chloride brine. However, the sodium chloride was difficult to remove from the gel-like precipitate by washing. Because of the likelihood of sodium chloride contamination of the regenerated leachant and the treated coal, no further work was done on this approach.

LEACHANT DESULFURIZATION WITH LIME

To investigate the possibility of exploiting the cost advantage of utilizing lime, a set of experiments was run on the desulfurization of oxidized leachant with lime. In the initial experiments, a synthetic solution made up with Na_2SO_4-NaOH was used. One experiment was run with spent coal leachant. The experimental conditions and results of the experiments are summarized in Table 3.F-6. The expected and/or desired chemical reactions were:

Leachant oxidation -- $S^{--} + 2O_2 \rightarrow SO_4^{--}$

Lime treatment -- $SO_4^{--} + \underline{CaO} \rightarrow CaSO_4 + 2OH^-$.

In the strong base of the leachant solution, the following competing reaction is possible:

$$Ca^{++} + 2OH^- \rightarrow \underline{Ca(OH)}_2$$

Results of the experiments in Table 3.F-6 suggest that all calcium had precipitated (presumably by the last reaction) since all remained in solution in the leachant. Thus, this regeneration scheme would produce a continual buildup of sulfate in the recycled leachant and therefore is considered unsatisfactory.

LEACHANT DESULFURIZATION WITH COPPER

Consideration was given to the use of copper for the desulfurization of leachant. As is indicated by the known chemistry, copper can be taken into basic solution by formation of the ammonia complex:

$$Cu + NH_3 + H_2O \xrightarrow{O_2} Cu(NH_3)_4^{++} + 2OH^-$$

$$\text{or} \quad Cu + NH_3 + H_2O \xrightarrow{O_2} Cu(NH_3)_2 + OH\ .$$

This was checked in the laboratory, but the maximum concentration of copper that could be put into solution was not determined.

The copper in solution can be added to the leachant in just stoichiometric proportions to precipitate the sulfide sulfur:

$$Cu(NH_3)_4^{++} + S^{--} \rightarrow \underline{CuS} + 4NH_3\uparrow$$

$$\text{or } 2\ Cu(NH_3)_2^{+} + S^{--} \rightarrow \underline{Cu_2S} + 4NH_3\uparrow\ .$$

The solubility products for the copper sulfides are extremely low:

$$[Cu^{++}][S^{--}] = 8.5 \times 10^{-44}$$

$$[Cu^{+}]^2[S^{--}] = 2 \times 10^{-47}\ .$$

These are more than 20 orders of magnitude lower than that for zinc sulfide, and correspondingly lower solubility and very low retention of copper and sulfur in the leachant can be expected.

TABLE 3.F-6. SUMMARY OF EXPERIMENTS ON THE DESULFURIZATION OF OXIDIZED LEACHANT WITH LIME

Experiment	Solution/Conditions of Treatment	Analysis Total Sulfur
	Synthetic NaOH-Na_2SO_4 solution	0.22
18-86	Treated with 5xCaO[(a)], 20 C, 184 hr	0.21
18-87	Treated with 5xCaO, 95 C, 64 hr	0.21
	Diluted (x2) synthetic NaOH-Na_2SO_4 solution	0.11
18-89A	Treated with 5xCaO, 95 C, 16 hr	0.12
18-89B	Treated with 10xCaO, 95 C, 16 hr	0.12
	Diluted (x4) synthetic NaOH-Na_2SO_4 solution	0.055
18-90A	Treated with 5xCaO, 95 C, 16 hr	0.06
18-90B	Treated with 10xCaO, 95 C, 16 hr	0.06
	Leachant 33018-53-18	0.30
18-88A	Treated with 5xCaO, 95C, 24 hr	0.36
18-88B	Treated with 10xCaO, 95C, 24 hr	0.28

(a) i.e., 5 times the Ca required to react with the sulfate present to form $CaSO_4$.

The copper can be regenerated by a gas/solid reaction with hydrogen that presents no separation problems, leaves the copper in a very finely divided state for reuse, and yields sulfur in the tractable hydrogen sulfide form:

$$CuS + H_2 \rightarrow Cu + H_2S\uparrow$$

$$\text{or } Cu_2S + H_2 \rightarrow 2Cu + H_2S\uparrow.$$

This also was checked in the laboratory using cupric sulfide, the reaction was observed to begin as temperature was raised into the range just above 400 C; the reaction was noted to yield copper at temperatures less than 740 C.

For investigation of the desulfurization of leachant with copper, copper (powder) was taken into solution in aqueous ammonia. Using procedures similar to those described in the previous section, the leachant was treated with the copper solution at elevated temperature (∿90 C). The results show that good sulfide extraction was obtained--85 to 90 percent. However, the results also show that total sulfur concentration was high, with 59 percent of the initial concentration remaining --presumably due to reactions that produce oxidized forms of sulfur.

Thus, there appear to be some complications in the form of side reactions associated with the use of copper for leachant regeneration.

APPENDIX 3-G

SUPPORTING MATERIAL FOR LEACHANT REGENERATION:

INVESTIGATION OF OTHER APPROACHES TO THE RECYCLE OF IRON VALUES

From the standpoint of economics and environmental impact, the most desirable thing would be to recycle the iron values in the precipitated iron sulfide by converting to active hydrated iron oxide, precipitated in aqueous solution. Key requirements of such a recycle process would be the evolution or removal of the sulfur in the sulfide or elemental state and the use of low-cost materials. A number of iron recycle schemes were devised and several, in addition to those discussed in the main body of the report, were investigated experimentally.

REGENERATION OF IRON HYDROXIDE WITH OXYGEN AND LIME

When the leachant is desulfurized with excess iron hydroxide, a mixture of iron hydroxide and iron sulfide results. This "spent" iron hydroxide can be separated from the leachant by filtration and can be treated for reuse as is indicated by the following set of reactions:

Leachant regeneration -- $Fe(OH)_2 + S^{--} \rightarrow \underline{FeS} + 2OH^-$

Sulfur oxidation -- $\underline{FeS} + 2\ O_2 \underset{H_2}{\rightarrow} FeSO_4$

Lime treatment -- $FeSO_4 + CaO \rightarrow \underline{CaSO_4} + \underline{Fe(OH)_2}$

Leachant regeneration -- $\underline{Fe(OH)_2}/\underline{CaSO_4} + S^{--} \rightarrow \underline{FeS/CaSO_4} + 2OH.$

The mixture of $DeSO_4/CaSO_4$ resulting from the lime treatment can be used to desulfurize additional leachant (as shown in the last reaction) providing the following undesired reaction is sluggish or is not favored:

$$CaSO_4 + 2OH^- \rightarrow Ca(OH)_2 + SO_4^{--}.$$

Solubility data for the compounds which are given in the following tabulation show that in the absence of high concentration of hydroxyl ion, the precipitation of calcium sulfate in preference to that of calcium hydroxide is possible. For example, note that the concentration of calcium ion from calcium hydroxide exceeds that required to precipitate the sulfate (except near 100 C).

		Solubility per 100 ml of Water		
Compound	MW	grams	g-moles of compound = g-ions of Ca^{++}	Temp, C
$CaSO_4 \cdot 2H_2O$	172	0.241	0.0014	0
		(0.236)	(0.00137)	25
		0.222	0.0013	100
$Ca(OH)_2$	73	0.185	0.0025	0
		(0.158)	(0.0021)	25
		0.077	0.0010	100

Initial exploratory experiments utilizing ferrous sulfate confirmed that lime precipitates calcium sulfate and ferrous hydroxide from a ferrous sulfate solution as is indicated by the "lime-treatment" equation above.

A series of experiments was run to assess the potential of this regeneration scheme. Data on the experiments, which are given in Table 3.G-1, show that good reductions of sulfide concentrations in the leachant were obtained. However, total sulfur analyses on selected samples show that sulfur concentrations were high in the treated leachant, presumably due to the following reaction involving the strong hydroxide of the leachant:

$$\underline{CaSO_4} + 2OH \rightleftarrows \underline{Ca(OH)_2} + SO_4^{--}.$$

Thus, this regeneration scheme appears to be unsatisfactory because of the high sulfate concentrations left in the treated leachant.

REGENERATION OF IRON HYDROXIDE WITH SULFURIC ACID AND LIME

Several exploratory experiments were run on the potential sequential use of the low-cost reagents sulfuric acid and lime for leachant regeneration. The expected reactions involved are the following:

TABLE 3.G-1. SUMMARY OF EXPERIMENTS ON REGENERATION OF LEACHANT WITH $Fe(OH)_2/CaSO_4$

			Analysis	
Experiment	Solution/$Fe(OH)_2$-$CaSO_4$ Treatment		S^{--}, g/l	Total S, wt %
	Initial leachant		2.46	0.26 (∿2.86 g/l)
21-6	Leachant treated with quantity containing 23.7 times stoichiometric Fe (dried)	30 min 60	0.42 0.54	2.65
21-7	Leachant treated with quantity containing 23.7 times stoichiometric Fe (from dilute solution -- dried)	30 min 60	1.16 1.06	
21-13	Leachant treated with quantity containing 3 times stoichiometric Fe (dried)	30 min 60 min	0.72 0.64	
21-19	Leachant treated with quantity containing 10 times stoichiometric Fe (not dried)	30 min 60 min	1.04 0.87	
21-23	Leachant treated with quantity containing 20 times stoichiometric Fe (not dried)	30 min 60 min	0.01 0.08	0.14 (∿1.54 g/l)
	Analysis of residual solid: Ca = 0.16 wt %, SO_4 = 1.77 wt %			

Leachant regeneration -- $\underline{\mathrm{Fe(OH)}}_2/\underline{\mathrm{CaSO}}_4 + \mathrm{S}^{--} \rightarrow \underline{\mathrm{FeS/CaSO}}_4 + 2\mathrm{OH}^-$

Iron hydroxide regeneration -- $\left\{\begin{array}{l} \underline{\mathrm{FeS/CaSO}}_4 + 4\mathrm{H_2SO_4} \rightarrow \underline{4\mathrm{S}} + 3\mathrm{FeSO_4} + \\ \quad 3\mathrm{CaSO_4} + 4\mathrm{H_2O} \\ 3\mathrm{FeSO_4} + 3\mathrm{CaO} \xrightarrow{\mathrm{H_2}} \underline{3\mathrm{FeSO}}_4/\underline{\mathrm{CaSO}}_4. \end{array}\right.$

The second of the reactions in which elemental sulfur is precipitated by reacting sulfide and sulfate sulfur in the presence of ferrous iron was confirmed. The sulfur then was separated from the solubilized iron values by filtration prior to reprecipitating the iron.

Since this regeneration scheme also would result in build-up of sulfate in the leachant (such as that discussed in connection with the regeneration of oxidized leachant with lime), work was discontinued on this method when that drawback was confirmed.

REGENERATION OF IRON HYDROXIDE WITH ACETIC ACID

In several exploratory experiments, it was found that acetic acid at elevated temperature under reflux slowly dissolved the iron sulfide giving a clear, deep reddish-brown solution which, under hydrolysis, yielded voluminous hydrated iron oxide.

The reaction was very slow. In addition, an estimate based on the theoretical consumption of acetic acid indicated that the cost would be too high for commercial process use. Thus, work on this approach was abandoned following the exploratory work that outlined requirements.